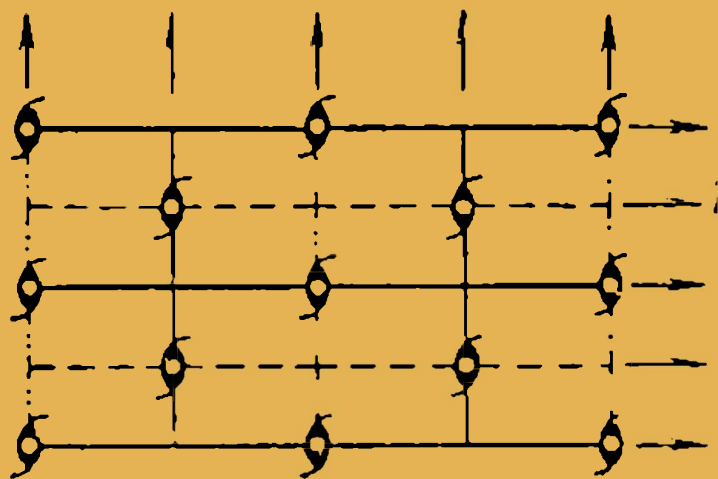


E. A. TUROV

*Physical Properties of
Magnetically Ordered
Crystals*



PHYSICAL PROPERTIES
OF MAGNETICALLY ORDERED CRYSTALS

Physical Properties of Magnetically Ordered Crystals

E. A. TUROV

Translated from the Russian by SCRIPTA TECHNICA, Inc.

Translation edited by
A. TYBULEWICZ

PHYSICS ABSTRACTS, LONDON

and

S. CHOMET

KING'S COLLEGE, LONDON



1965

ACADEMIC PRESS New York and London

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ACADEMIC PRESS INC.

111 FIFTH AVENUE

NEW YORK, NEW YORK 10003

United Kingdom Edition

Published by

ACADEMIC PRESS INC. (LONDON) LTD.

BERKELEY SQUARE HOUSE, LONDON W. 1

Library of Congress Catalog Card Number: 64-66185

Originally published by the Academy of Sciences of the USSR, Moscow, 1963
under the title:

FIZICHESKIYE SVOYSTVA MAGNITUPORYADOCHENNYKH KRISTALLOV

Fenomenologicheskaya teoriya spinovykh voln v ferromagnetikakh,
antiferromagnetikakh i slabykh ferromagnetikakh

by

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PRINTED IN THE UNITED STATES OF AMERICA

Preface

The purpose of this book is to present a phenomenological theory of spin waves in ferromagnets, antiferromagnets, and weak ferromagnets. A systematic account of the problems arising in the modern theory of the magnetically ordered state in solids (ferromagnets and antiferromagnets) has not been attempted. Rather, the book is intended for readers acquainted with the principal methods and results of this theory, and the primary aim is to consider a wide range of various physical phenomena in ferromagnets and antiferromagnets using a unified phenomenological method based on the spin-wave theory and on the nature of these phenomena and the symmetry properties of crystals. Within the framework of this method, an attempt is made to establish qualitative and quantitative relationships reflecting the fundamental connections between the very different effects in ferromagnets and antiferromagnets. Obviously, such theoretical relationships are of the greatest interest in connection with experimental verification of the initial assumptions of the majority of modern theories of ferromagnetism and antiferromagnetism.

Within the framework of the phenomenological method, effects related to weak ferromagnetism in antiferromagnetic crystals are treated fully and systematically. Studies of these effects are of fundamental importance to the theory of ferromagnetism and antiferromagnetism in general.

Since the book is essentially a review supplemented by a description of the work carried out by the author (alone or in conjunction with others) it is not a complete presentation of all the problems actually considered. For this reason, the literature cited includes only the work to which reference was essential.

The book would not have appeared but for the cooperation of the author's colleagues at the Theoretical Physics Division of the Metal Physics Institute, Academy of Sciences of the USSR, directed by S. V. Vonsovskiy. The author would like to take this opportunity to express his gratitude for their generous assistance.

E. A. Turov

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Introduction

Crystals can be divided into two large groups with regard to their magnetic properties: substances possessing ordered atomic magnetic structures (ferromagnets and antiferromagnets) and substances without such structures (paramagnets and diamagnets). In the latter case, there is ordering only in the mass density space $\rho(x, y, z)$ and the charge density space $e(x, y, z)$, which are periodic functions of spatial coordinates. In the former case the ordering of the atoms or ions in a crystal has superimposed on it the ordering of the magnetic moment orientations of the atoms or ions so that a vector function of the magnetic moment density $M(x, y, z) \equiv M(\mathbf{r})$ is also periodic in space.* Such a spatially periodic distribution of the magnetic moments throughout the lattice sites will be called a *magnetocrystalline structure* (or, simply, a magnetic structure). The normal crystal structure, in which only the chemical nonequivalence of the various lattice sites is allowed for, will be called a *crystallochemical structure*.

The present work deals with theoretical investigations of various properties of magnetic substances exhibiting a magnetocrystalline structure.

For a given crystallochemical structure, a crystal may, in general, have many types of magnetocrystalline structure. The number of possible types of magnetocrystalline structure and their symmetry in a given crystal are determined wholly by the symmetry properties of the crystallochemical lattice. The appearance

*From the microscopic point of view, the meaning of $M(\mathbf{r})$ is as follows:

$$M(\mathbf{r}) = \frac{1}{V} \sum_n \langle \mu_n \rangle_t \delta(\mathbf{r} - \mathbf{r}_n),$$

where $\langle \mu_n \rangle_t$ is the time-average of the magnetic moment of an atom at a site whose coordinates are \mathbf{r}_n in a crystal lattice; the summation is carried out over all lattice sites in a crystal of volume V ; the δ function expresses the discrete nature of the distribution of magnetic moments in a crystal.

in a magnetic crystal of an additional characteristic—the magnetic moment density $M(\mathbf{r})$ —can only reduce the crystal symmetry compared with its nonmagnetic state. Each of the symmetry transformations which can make the magnetocrystalline structure coincide with itself should necessarily be contained in the symmetry operations which describe the crystallochemical structure.* Here, we mean the total symmetry of a lattice including all rotations and reflections, the infinite discrete set of all possible parallel translations, and another symmetry element which represents the properties of the system with regard to the change of the sign of time ($t \rightarrow -t$) [1]. The axial vector $M(\mathbf{r})$ reverses its direction after this transformation, in analogy with the angular velocity vector.**

The transformation $t \rightarrow -t$ (usually denoted by R) is an independent symmetry element in crystals which do not possess a magnetocrystalline structure, and whose symmetry is identical with the crystallochemical structure. Then, after the transformation R , the distribution of magnetic moments may coincide with the initial one, i.e., $M(\mathbf{r}) \rightarrow M(\mathbf{r})$, but on the other hand it follows from the general property of $M(\mathbf{r})$ with respect to R that $M(\mathbf{r}) \rightarrow -M(\mathbf{r})$. Consequently, in substances which do not have a magnetocrystalline structure, $M(\mathbf{r}) \equiv 0$. The latter may apply to crystals composed of nonmagnetic atoms ($\mu_n = 0$) or when the orientations of magnetic moments of all atoms vary at random with time so that $\langle \mu_n \rangle_t = 0$.

It follows also that in the magnetocrystalline structure [when $M(\mathbf{r}) \neq 0$] the transformation R cannot by itself be a symmetry element of a crystal. However, it may be combined with other transformations (radiation, reflection, or translation) in complex symmetry elements.

Thus, if we know the crystallochemical structure of a magnetic substance we can, in principle, calculate all the possible types of magnetocrystalline structure permitted by the crystal symmetry, indicating that set (group) of symmetry elements (taken from all the symmetry elements of the initial crystallochemical structure, including the transformation R) for each type of magnetic ordering represented by such a set.***

The problem as to which of the possible magnetocrystalline structures should be realized in a given substance with known

*In group-theoretical language, this means that a group of symmetry transformations for each possible magnetocrystalline structure should be a subgroup of the symmetry group of the initial crystallochemical structure.

**The magnetic moment can be expressed in the form of a vector product of a current $j(\mathbf{r})$ and the radius vector \mathbf{r} : $M = [\mathbf{r} \cdot \mathbf{j}]$ since $\mathbf{j} \rightarrow -\mathbf{j}$ when $t \rightarrow -t$; therefore, simultaneously, $M \rightarrow -M$.

***All 230 crystal (nonmagnetic) space groups allow in total 1651 magnetocrystalline (or, simply, magnetic) space groups [2].

crystallochemical structure cannot be elucidated simply from symmetry considerations. The actual type of crystallomagnetic structure is determined by the nature and magnitude of spin interaction between atoms and ions, of which a magnetic crystal is composed. The spin interactions (i.e., the interactions which depend on the magnitude and direction of atomic spins with respect to one another or with respect to the crystal axes) can be divided into two types in accordance with their role in the establishment of one or another of the actual magnetocrystalline structures. One type is the exchange interactions of electrostatic origin, responsible for the phenomenon of magnetic ordering itself. The characteristic feature of exchange forces is their isotropic nature, in the sense that they are independent of the spin direction with respect to the crystallographic axes.* However, the energy of the exchange interaction between any two atoms depends on the mutual orientation of their spins, leading finally to a definite distribution of magnetic moments in a lattice which represents the minimum of the free exchange energy of the whole crystal.

Depending on the relationship between the absolute values and signs of the exchange interaction parameters ("exchange integrals") this ordering may be either ferromagnetic or antiferromagnetic. In a ferromagnet, the total magnetic moment in each magnetocrystalline unit cell is not equal to zero, but in an antiferromagnet this moment is zero. We must stress that we are speaking of magnetocrystalline unit cells, which represent the periodic repetition of the crystallomagnetic structure. Since atoms that are equivalent in the crystallochemical structure may become non-equivalent in magnetic ordering (because of different directions of their magnetic moments) the magnetocrystalline unit cell should be larger, by an integral factor, than the crystallochemical unit cell.

The isotropic exchange forces do not give rise to any definite orientation of different magnetic moments with respect to the crystallographic axes but they produce mutual ordering of the spins at various lattice sites. The fact that the ordered distribution of the spins is always oriented in a definite way with respect to the crystal axes is due to forces of another type: relativistic or magnetic forces (spin-spin dipole, quadrupole, etc.; spin-orbital; orbital-orbital). Magnetic interactions are responsible for the existence of the magnetocrystalline anisotropy which is manifest in the dependence of the crystal energy on the orientation of the magnetic moments of the atoms with respect to the

*This does not necessarily mean that exchange interactions are independent of the direction of the radius vector joining the atoms being considered.

crystallographic axes. We can say that in a crystal there are effective internal magnetic fields which tend to orient magnetic moments along certain directions. This field may alter somewhat the mutual orientation of the magnetic moments of atoms, thus distorting to a certain extent the magnetocrystalline structure due to exchange forces. This, in particular, may give rise to a spontaneous resultant magnetization in an antiferromagnetic crystal so that such a crystal can no longer be regarded as an antiferromagnet ("weak ferromagnetism"). However, the second of these effects is as a rule small, because the magnetic interactions causing it are usually weak compared with the exchange (electrostatic) interactions between magnetic atoms.* Therefore, "weak ferromagnets" behave in many respects like normal antiferromagnets. The magnetocrystalline anisotropy determines, in fact, all the observed magnetic properties of a crystal with a given magnetocrystalline structure (behavior in an external magnetic field, nature of the magnetization curves, magnetic resonance absorption, etc.).

Ferromagnetism and antiferromagnetism are collective properties of a system of a large number of electrons in a crystal. Hence, the development of a consistent quantum-mechanical theory of these phenomena meets with considerable difficulties as in any other multielectron theory. The available microscopic theories of ferromagnetism and antiferromagnetism originating in the work of Frenkel [3] and Heisenberg [4] are based on rough simplified models. Nevertheless, these theories allow us to understand fully the qualitative aspects of the observed phenomena.

In some cases, it has been possible to determine in detail the nature of the forces responsible for the magnetic ordering itself. In fact, ferromagnetism and antiferromagnetism occur not only in pure transition elements but also in a great variety of compounds and alloys in which these elements are present. Therefore, the actual exchange interaction mechanism responsible for the ordered distribution of the magnetic moments of atoms in a crystal can vary considerably from substance to substance. We can have both the direct exchange interaction between electrons of the inner unfilled shells of neighboring magnetic atoms, as well as various types of the indirect exchange interaction in which electrons of the valence shells of nonmagnetic atoms and of magnetic atoms take part. Finally, the exchange interaction between magnetic atoms in metals and alloys may involve the collective state of conduction electrons. However, irrespective of their nature, exchange forces

*We note, however, that in some cases—for example, rare-earth metals—the magnetic (spin—orbital) interactions may sometimes strongly affect the nature of the magnetic ordering.

have certain features which are important in theoretical considerations. We have already mentioned the isotropic nature of these forces. Another important characteristic is the fact that the exchange interactions almost always decrease very rapidly with distance (short-range forces). Obviously, only the exchange interaction via conduction electrons can, under certain conditions, be long-range.*

Microscopic models of various magnetic interactions have shown that, in the majority of cases, the spin-orbital interaction is the basic one in the magnetocrystalline anisotropy. It relates the directions of the spin magnetic moments of atoms through their orbital states with the crystallographic axes. However, irrespective of the microscopic nature of the magnetic anisotropy forces, their macroscopic manifestation in a crystal is determined mainly (at least qualitatively) by the type of symmetry of the lattice.

Thus various microscopic models of ferromagnetism and antiferromagnetism, in spite of their approximate nature, have led to the establishment of general ideas on the nature of these phenomena, which are independent of the models themselves. Here, naturally, the question arises of how far one can describe and explain various actual properties of magnetic crystals by means of the foregoing general descriptions of the nature of the forces responsible for the magnetic ordering and magnetic anisotropy, and of the properties of the crystallochemical and magnetocrystalline symmetry, without using model representations. The answer to this question can be obtained by using the phenomenological method of investigating ferromagnetic and antiferromagnetic phenomena.

The purpose of the present book is to consider theoretically a large number of very different properties of magnetic materials with different types of magnetocrystalline structure using the unified phenomenological approach. The phenomenological method was first used by Weiss [5] in his classical theory of magnetism based on the idea of an internal molecular field; the exchange nature of this field was established by Frenkel [3] and Heisenberg [4]. This method was then used successfully by Van Vleck [6] and Néel [7], who extended the molecular field theory to antiferromagnets and ferrites. The molecular field theory, in spite of its rough qualitative nature, explained the principal magnetic properties of ferromagnets and antiferromagnets, especially after Akulov developed his phenomenological theory of the magnetocrystalline anisotropy [8].

*This may explain the existence of magnetic ordering in some dilute solutions with very small concentrations of magnetic atoms, as well as specific types of magnetic ordering (helical structures, etc.) observed in rare-earth metals.

From the quantum mechanical point of view, the molecular field method is equivalent to the method of the center of gravity for the energy, in which the energy of a ferromagnet is calculated on the assumption that it depends only on the average magnetization in a crystal and is independent of the magnetic moment distribution in the interior of this crystal.* These methods correctly reflect the nature of the behavior of magnetic crystals, but they do not give good quantitative agreement with experiment. This is particularly true at low temperatures where the dominant agent is that fraction of the crystal energy related to inhomogeneous oscillations of the magnetization (spin waves).

In the physical and mathematical senses, the most rigorous approach is the phenomenological one based on the thermodynamic theory of phase transitions in crystals, developed by Landau and Lifshits [1, 9]. The method was used by Vonsovskiy [10] and Ginzburg [11], who studied phase transitions of the second kind in ferromagnets. Even earlier (in 1933), Landau himself used this method to investigate antiferromagnetic transitions in dichlorides of transition metals [12]. In this work, Landau first put forward the idea of antiferromagnetism as a special magnetically ordered state, separated from the paramagnetic state by a phase transition point. Later, the thermodynamic theory of the properties of an antiferromagnet near the antiferromagnetic Curie point was extended by Belov and Levitin [13].

The advantage of the Landau method is its thermodynamic basis and the use of symmetry properties. Its power was demonstrated in the work of Dzyaloshinskiy [14], who explained the physical nature of weak ferromagnetism by showing it to be an intrinsic property of antiferromagnetic crystals of a certain symmetry. Nevertheless, the thermodynamic method does not explain all the properties of magnetic crystals: in particular, it fails to account for the properties which require a knowledge of the energy spectrum of the system. Among such properties are, for example, temperature dependences of various physical properties both at equilibrium (specific heat, magnetic susceptibility, magnetization, anisotropy constants, etc.) and under dynamic conditions (relaxation times, electrical conductivity, thermal conductivity, etc.). Only close to the Curie point does the theory of phase transitions of the second kind give definite limiting relationships for the temperature dependence of some of these quantities.**

*In the case of antiferromagnets and ferrites, it is assumed that the crystal energy is determined only by the average values of the magnetization of magnetic sublattices in a given magnetocrystalline structure [44].

**We shall not consider here the difficulties in the Landau theory in connection with the validity of the expansion of the thermodynamic potential in the region of the Curie point using ordering parameters (sublattice magnetizations) [1].

To determine the energy spectrum of a magnetic substance, it is necessary to solve in some way the mechanical (classical or quantum) problem of free vibrations of a system of spins. The consistent solution of this problem is possible only in the case of weak oscillations of the system, using the so-called spin-wave approximation convenient for the description of the properties of magnetic crystals at temperatures which are low compared with the Curie point. However, even within the framework of the spin-wave approximation, both the phenomenological and microscopic model approaches are possible. In the former, the spin-wave theory is based on the phenomenological Hamiltonian, derived from considerations of the invariance of its terms under symmetry transformations, and from electromagnetic field equations in a magnetic medium.

The fundamentals of the phenomenological theory of spin waves in its classical form were given in the work of Landau and Lifshits [15]. Herring and Kittel were the first to use this method to calculate the spin-wave spectrum allowing for magnetic interactions [16]. Later, the method was used by many workers, including the author of this book, to describe various individual properties of ferromagnets and antiferromagnets. In particular, we must mention the numerous papers of the Khar'kov physicists—Akhiezer, Kaganov, Tsukernik, Bar'yakhtar, and others*—as well as the work of Kittel and Abrahams [18], and Ament and Rado [19]. Very important methodological studies were carried out by Bogolyubov and Tyablikov [20], who developed the method of approximate second quantization and applied it to the spin-wave theory. Later, they also developed a quantum-statistical method of Green's temperature functions [77] for problems in the theory of ferromagnetism and antiferromagnetism.

The phenomenological theory of spin waves is the main tool in the present review. This method is developed and used here for magnetic substances with various types of ordering (ferromagnets and ferrites, antiferromagnets and weak ferromagnets), taking into account their actual magnetocrystalline structure. Very different properties of the same magnetic substance are discussed simultaneously and compared, e.g., the magnetic and magnetoresonance properties, magnetoelastic and thermal properties. This approach gives, in many cases, simple and very general (within the framework of the approximations used) relationships between various physical properties of a magnetic substance easily checked by experiment.

*A complete bibliography of the work up to 1960 is given in the review paper of Akhiezer, Bar'yakhtar, and Kaganov [17].

We shall note four important limitations which will be accepted throughout this book.

First, we shall assume that a coherent magnetocrystalline structure extends throughout a crystal. In other words, we shall not consider effects connected with the existence of boundaries between different magnetically ordered regions (domains). The effects due to the presence of domain structure in ferromagnets and antiferromagnets are a special subject and will not be considered here.

Second, we shall not consider any of the properties of ferromagnets and antiferromagnets involving conduction electrons. Therefore, the present work applies, strictly speaking, to poorly conducting magnetic substances (dielectrics and semiconductors). However, it can be applied to metals as well if conduction electrons are not active in the ferromagnetic and antiferromagnetic phenomena.*

Third, we shall employ the widely used (although unjustified from the quantum-mechanical point of view, with the exception of the classical limiting case for which the atomic spin is $S \gg 1$) assumption of the ground state of an antiferromagnet based on the magnetic sublattice representation. We note that experimental verification of some of the results obtained in the present work should provide an answer to the limits of applicability of the "sublattice hypothesis."

Fourth, we shall consider only magnetocrystalline structures with collinear or weakly noncollinear distribution of the magnetic moments of the sublattices in the ground state, which makes it possible to consider, in most cases, only two "effective" magnetic sublattices. Noncollinear magnetocrystalline structures which cannot, in principle, be described by means of two magnetic sublattices (including helical structures, for which the sublattice concept loses its meaning altogether) will not be discussed. The only exception will be noncollinear structures (discussed in Chap. X) for which the noncollinearity of the magnetic moments is due to magnetic anisotropy forces, and which requires four magnetic sublattices to describe them.

We shall now consider in detail the plan of the book.

In Chapter I, we present—in general form—the phenomenological approach to ferromagnetic and antiferromagnetic phenomena, and discuss the main assumptions and approximations involved [21, 25–28]. In the same chapter (and in its appendix) we consider

*A phenomenological approach to the properties of conducting ferromagnets and antiferromagnets, allowing for the active role of conduction electrons, was developed in other papers by the present author [21–24], but will not be described here.

the problems relating to the number of magnetic sublattices needed to describe a magnetic crystal and the number of "acoustic" and "optical" branches of spin waves.

Chapter II deals with the spin-wave spectra and the principal thermodynamic properties of ferromagnets, using mainly the uniaxial crystals as an example [26, 28].

Chapter III is a development of Chapter II for crystals of arbitrary symmetry and magnetic anisotropy constants of any order. A general theory of the temperature dependence of the magnetic anisotropy constants of ferromagnets is developed [29], as well as a theory of the phenomena connected with isotropic and anisotropic magnetostriction [25, 30]. Several very general relationships are derived between the phenomenological parameters which describe these phenomena.

Chapter IV presents a theory of the resonance and thermodynamic properties of antiferromagnets at low temperatures [26, 28, 31]. Here, we discuss in detail the theoretically predicted relationships for the magnetization, magnetic susceptibility, and specific heat as a function of temperature, and the magnitude and direction of the magnetic field.

In Chapter V, general conditions are established for the existence of weak ferromagnetism in antiferromagnetic crystals [32-34]. A table and classification are given for all antiferromagnetic structures with weak ferromagnetism. The role of the anisotropy tensor of the gyromagnetic ratio in the phenomena of weak ferromagnetism is considered.

In Chapters VI, VII, and VIII, detailed consideration is given to magnetic properties of all the main types of the weak ferromagnet. The magnetization curves are calculated for absolute zero, the features of spin-wave spectra are considered, and the temperature dependence is discussed for each type of spontaneous magnetization and magnetic susceptibility arising in weakly ferromagnetic structures [35-40].

Chapter IX deals with magnetic resonance in weak ferromagnets [35-40]. Resonance frequencies are given for various types of weak ferromagnet as a function of the magnitude and direction of a constant magnetic (bias) field, and the corresponding high-frequency magnetic susceptibilities are calculated.

Throughout these nine chapters, only the collinear or weakly noncollinear magnetocrystalline structures of antiferromagnets and weak ferromagnets are discussed; the properties of these structures can be described by means of two crystallographically equivalent magnetic sublattices. Only such noncollinearity of the magnetic moments of the sublattices as leads to the appearance of weak spontaneous magnetization in an antiferromagnet is considered.

In Chapter X, actual examples of rhombic crystals with four magnetic ions in the unit cell are used to consider possible non-collinear magnetic structures requiring more than two magnetic sublattices to describe them [39]. An explanation is given of the role of possible noncollinearity of spins which does not give a resultant magnetic moment in a crystal.

Finally, in Chapter XI, the magnetic thermodynamic properties of crystals with two crystallographically unequivalent magnetic sublattices are discussed [35]. Attention is focused on ferromagnetism appearing due to the difference between the gyro-magnetic ratios of the sublattices and also due to the different temperature dependences of their magnetic moments.

A list is appended of the main qualitative and quantitative relationships obtained in this book and which require experimental verification.

CHAPTER I

General Phenomenological Approach to the Properties of Nonconducting Magnetic Crystals

1. MAGNETIC SUBLATTICES AND THE PHENOMENOLOGICAL HAMILTONIAN

Our aim is to investigate theoretically the macroscopic properties of magnetic crystals, taking into account their actual crystallographic structure. First, we have the problem of the method of describing a given magnetocrystalline structure and the number of macroscopic parameters needed for this description. A magnetocrystalline structure is described completely by assigning to each point in the crystal an intrinsic (microscopic) density of the magnetic moment $M(\mathbf{r})$ averaged only with respect to time. The vector function $M(\mathbf{r})$ may vary from one site to another even within the same unit, the magnetocrystalline cell. If we want to investigate the influence of the type of magnetic ordering on the observed macroscopic properties of a crystal, we introduce a magnetic moment density $M_j(\mathbf{r})$ for each magnetic sublattice separately (j is the number of the sublattice). A magnetic sublattice is taken to consist of magnetic atoms whose magnetic moments can be made to coincide by translatory operations included in the symmetry elements of the magnetocrystalline lattice. In other words, the number of magnetic sublattices is in general equal to the number of magnetic atoms in a unit magnetic cell whose magnetic moments cannot be made to coincide by these translations.

The magnetic densities $M_j(\mathbf{r})$ may be considered macroscopic parameters similar to the long-range order parameters in the theory of orderable alloys [41]. We can talk of their temperature dependence, magnetic field dependence, etc. These parameters,

which represent the type and degree of magnetic ordering, are determined in neutron diffraction experiments.

The phenomenological approach is based on the invariant expansion of the free energy (in the thermodynamic approach) or simply the energy of the Hamiltonian (in the mechanical approach) in terms of internal parameters representing the state of a system. To begin with, we shall assume that the state of a magnetic crystal is fully described by giving its magnetic densities $M_j(\mathbf{r})$ ($j = 1, 2, \dots, n$, where n is the number of the sublattice). These densities represent, depending on the approach, the average (thermodynamic) or intrinsic local magnetizations of the magnetic sublattices. The elastic state of the crystal will be considered later.

As already pointed out, these considerations are based on the spin-wave theory and apply mainly at low temperatures. We have to solve the mechanical problem of the ground (the energetically lowest) state and of the spectrum of free oscillations of local magnetizations $M_j(\mathbf{r})$. For reasons of convenience, we shall consider a magnetic crystal to be a continuous medium in which a given point is described by the values of n vector functions $M_j(\mathbf{r})$. The relationship between the discrete and continuous descriptions may be represented by

$$M_j(\mathbf{r}) = \sum_i^{(r)} \mu_i^{(j)} / v, \quad (1.0)$$

where $\mu_i^{(j)}$ is the magnetic moment of the i th ion in the j th sublattice, and the summation is carried out over all sites in a physically small volume v_j (around a point whose radius vector is \mathbf{r}) within which the moments $\mu_i^{(j)}$ can be considered to be equal for all values of i . Strictly speaking, the continuity of the medium is represented by the limit of (1.0) as $v \rightarrow 0$, with the ratio in the right-hand part kept constant.

The limitation imposed by the discrete distribution of the magnetic moments in space is that the minimum volume v for any sublattice j cannot be less than the volume v per unit site of this sublattice. Consequently, in the limiting case, the ratio in the right-hand part of (1.0) becomes $\mu_r^{(j)} / v_j$, where $\mu_r^{(j)}$ is the magnetic moment of one atom of the j th sublattice near point \mathbf{r} .

According to the continuous medium model, the ground state of a magnetic crystal (which corresponds to the thermodynamic equilibrium of the system at absolute zero) may be regarded as the state of uniform distribution of the magnetizations $M_j(\mathbf{r})$. In other words, in the ground state, $M_j(\mathbf{r}) = M_{j0}$, where M_{j0} is a vector constant in magnitude and direction throughout the whole sample. In classical theory, this vector is identical with the equilibrium magnetization of the j th sublattice at $T = 0^\circ\text{K}$.

Any departure from the uniformity of the magnetizations $M_j(\mathbf{r})$ leads to an increase in the energy of the magnetic crystal. The basic assumption of the phenomenological spin-wave theory is that only those oscillations of the vectors $M_j(\mathbf{r})$ are permitted for which the moduli of the vectors remain constant, i.e.,

$$M_j^2(\mathbf{r}) = M_{j0}^2, \quad (1.1)$$

and therefore any departure from the uniformity of the vectors $M_j(\mathbf{r})$ may only occur due to disorientation of their directions at various points.* This assumption is, in fact, equivalent to the condition of quasihomopolarity used in all microscopic theories in which the magnetic electrons are assumed to be localized near lattice sites.

The phenomenological Hamiltonian necessary for investigation of the ground state and the spin-wave spectrum of a magnetic crystal can be written from the most general considerations of the characteristic features of various types of force (exchange or magnetic) and their role in the phenomena of ferromagnetism and antiferromagnetism, and also from the requirement of invariance of each of the terms of the Hamiltonian under all crystal symmetry transformations.

All this can be formulated in a more concrete form.

a) Two types of terms can be distinguished in the Hamiltonian \mathcal{H} . There are terms of the isotropic exchange interaction responsible for the existence of an ordered magnetocrystalline structure over a certain range of temperatures. There are also terms due to the anisotropic magnetic interactions governing the equilibrium orientation of the magnetizations M_j with respect to the crystallographic axes.

b) In the presence of inhomogeneities of the functions $M_j(\mathbf{r})$, the Hamiltonian \mathcal{H} should depend not only on $M_j(\mathbf{r})$ but also on their space derivatives. One should distinguish two types of forces which raise the energy of a magnetic crystal because of inhomogeneities of $M_j(\mathbf{r})$. For short-range (exchange) forces, the energy density of inhomogeneities at any given point is determined by the derivatives of $M_j(\mathbf{r})$ only at that point, but for long-range (dipole, quadrupole, etc.) forces the increase of the energy density at each point is governed by the distribution of the inhomogeneities in the whole sample ("volume and surface demagnetizing fields").

c) The Hamiltonian of a magnetic crystal should be invariant with respect to all symmetry operations of the crystallochemical

*In the case of anisotropy of the gyromagnetic ratio tensor, (1.1) is replaced by similar conditions restricting the density of the sublattice momentum.

lattice; i.e., for all translations, rotations, and other (complex) transformations which make the crystal lattice coincide with itself, the energy of the crystal should remain constant. Under all these transformations, the location and direction of each elementary magnetic moment in a lattice can change only to an equivalent location and direction, since the energy of the crystal must remain constant. We stress once again that we are speaking here of symmetry transformations of the crystallochemical lattice, including the operation R by itself. The invariance of the Hamiltonian with respect to the transformation R , which reverses the directions of all the magnetizations M_j , means that the expansion of \mathcal{H} should include only terms of even powers of M_j .

d) To find the invariant expansion of the Hamiltonian \mathcal{H} in terms of magnetizations M_j , it is necessary to know the transformation properties of these magnetizations for all possible symmetry transformations of a given crystal. Among these properties are: first, the properties of each magnetization M_j separately, which are characteristic of axial vectors; secondly, transposition rules, for each symmetry operation, applying to the indices $j=1, 2, \dots, n$ of various M_j , which are determined by the actual positions of magnetic atoms in a lattice.*

e) Translations to a distance which is an integral multiple of the period of the magnetic unit cell leave all M_j unchanged. Therefore, these transformations yield no information which could be used to find \mathcal{H} as a function of M_j , and need not be considered.

We shall now write the energy density $\mathcal{H}(\mathbf{r})$, depending on the distribution of the magnetizations $M_j(\mathbf{r})$, in its most general form without yet specifying the type of crystal lattice:

$$\begin{aligned} \mathcal{H}(\mathbf{r}) = & A_{\alpha\beta}^{ij} m_{j_1\alpha} m_{j_2\beta} + B_{\alpha\beta\gamma\delta}^{ijkl} \frac{\partial m_{j_1\alpha}}{\partial r_\gamma} \frac{\partial m_{j_2\beta}}{\partial r_\delta} + \\ & + C_{\alpha\beta\gamma\delta}^{ijkl} m_{j_1\alpha} m_{j_2\beta} m_{j_3\gamma} m_{j_4\delta} + \dots - \frac{1}{2} \sum_{j_1 j_2} M_{j_1} H_{j_2} - \sum_j M_j H. \end{aligned} \quad (1.2)$$

Here, the summation is carried out over all double indices; the Greek indices α, β , etc., take the three values x, y , and z , while each of the indices j represents the sequential numbers of the magnetic sublattice: $1, 2, \dots, n$.

*Transposition of the indices of M_j is the result of the transposition of magnetic atoms by the appropriate symmetry operation. This transposition should be identical, i.e., the indices should remain unchanged if a given symmetry operation transposes atoms within the same magnetic sublattice. Conversely, if a given transformation relates to atoms in different sublattices (j and j') then the sequential numbers of these sublattices are interchanged and therefore the indices of the corresponding magnetizations M_j and $M_{j'}$ are transposed.

The total Hamiltonian of the system is an integral of $\mathcal{H}(\mathbf{r})$ over the whole volume of the crystal:

$$\mathcal{H} = \int_V \mathcal{H}(\mathbf{r}) d\mathbf{r}. \quad (1.3)$$

In expression (1.2), we used the notation

$$m_{j\alpha} = \frac{M_{j\alpha}}{M_{j0}},$$

where M_{j0} is the maximum projection of the vector \mathbf{M}_j along the quantization axis of this vector (M_{j0} can be considered the modulus of the equilibrium classical magnetization vector \mathbf{M}_{j0}). Finally,

$$H_j = -\nabla \left\{ \int_V \frac{-\operatorname{div} \mathbf{M}_j(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + \oint_{\Sigma} \frac{\mathbf{M}_j(\mathbf{r}') d\boldsymbol{\sigma}'}{|\mathbf{r} - \mathbf{r}'|} \right\}. \quad (1.4)$$

The second integral is taken over the sample surface Σ .

We shall now consider in more detail the characteristics and physical meaning of the terms in (1.2). The terms with the tensor coefficients A, B, C, \dots represent the short-range part of the energy density $\mathcal{H}(\mathbf{r})$, depending only on the values of the magnetizations $\mathbf{M}_j(\mathbf{r})$ and their derivatives at the point \mathbf{r} . The coefficients A, B, C, \dots are independent of the coordinates and are the phenomenological parameters of the theory. The number of non-zero independent components of each such tensor is determined by the crystal lattice symmetry. Their actual form is found from the invariance of $\mathcal{H}(\mathbf{r})$ under all crystallochemical symmetry operations. We can distinguish isotropic (exchange) terms among the coefficients referred to above. For example, we shall now write such terms for the first and second sums in (1.2); they are

$$A^{i_1 i_2} \mathbf{m}_{i_1 \alpha} \mathbf{m}_{i_2 \alpha} \quad \text{and} \quad B_{\gamma \delta}^{i_1 i_2} \frac{\partial m_{j_1 \alpha}}{\partial r_\gamma} \frac{\partial m_{j_2 \alpha}}{\partial r_\delta}. \quad (1.5)$$

This example shows that to separate out the exchange interaction terms in (1.2), it is necessary, in each of the sums, to make the signs of summation of pairs of $\alpha, \beta, \gamma, \delta$, etc., identical, and to assume that the corresponding coefficients A, B , etc., are independent of these signs. That is to say, it is necessary to select from the sums those terms in which \mathbf{M}_j are combined in pairs into "scalar products" (this is logical because the isotropic

terms should be independent of the directions of M_j with respect to the crystallographic axes). The remaining terms in the short-range part of $\mathcal{H}(\mathbf{r})$ represent, as a rule, the relatively low magnetic anisotropic energy (related to spin-spin, spin-orbital, etc., magnetic interactions of microparticles in a magnetic material), the order of smallness of such terms increasing with the number of $M_{j\alpha}$ pairs which are not converted into scalar products in these terms.*

The penultimate term in (1.2) gives the magnetostatic long-range part of the energy density related to the demagnetizing fields of the volume and surface "magnetic charges." In the expression (1.4), which defines these fields, the first term gives the internal demagnetizing field of the volume "magnetic charges," and the second term the demagnetizing field of the surface "magnetic charges." Fields H_j , of the same form as in (1.4), are the solutions of the equations of electrodynamics in the quasistationary approximation:**

$$\operatorname{rot} H_j = 0, \quad \operatorname{div} H_j = -4\pi \operatorname{div} M_j. \quad (1.6)$$

Finally, the last term in (1.2) gives the energy of a magnetic crystal in an external field H .

We note that expression (1.2) can be also regarded as the thermodynamic potential of a magnetic crystal, if the M_j are understood to represent not the local magnetizations of the sublattices but their average thermodynamic values. Then the coefficients A, B, C, \dots in (1.2) should be regarded as functions of the state of the system (i.e., as functions of temperature, pressure, and other internal parameters on which the state of the system depends). Such a thermodynamic potential may serve as the basis of an investigation of the properties of a magnetic crystal using Landau's theory of phase transitions.

*Because of the relativistic nature of magnetic interactions, these terms represent an expansion in terms of the small parameter v_0^2/c_0^2 , where v_0 is the velocity of an electron in a crystal and c_0 is the velocity of light.

**However, it should be noted that, in general, the problem of oscillations of magnetizations M_j should be solved simultaneously with the problem of the propagation of electromagnetic waves in a magnetic medium. We should start from the complete Maxwell equations with displacement currents allowing for the finite velocity of light c_0 . The quasistationary equations (1.6) should be used when the phase velocity of the complex spin-electromagnetic waves is low compared with the velocity of light in the medium, i.e., when

$$\frac{\omega}{k} \ll \frac{c_0}{\sqrt{\epsilon}}, \quad (1.7)$$

where ω and k are, respectively, the frequency and wave vector of these waves, and ϵ is the permittivity of the medium. In problems which are of interest to us, condition (1.7) is usually satisfied.

2. GENERAL FORMULATION OF THE SPIN-WAVE THEORY

The problem of determining the ground state and the spectrum of natural frequencies of small oscillations of a system, the energy density of which is given by the phenomenological expression (1.2), can be approached in two ways: classically and quantum-mechanically.

The classical approach is based on the solution of the equations of motion of classical magnetization $\mathbf{M}_j(\mathbf{r})$. When the condition (1.1) is satisfied, these equations are

$$\dot{\mathbf{M}}_j = -\gamma_j [\mathbf{M}_j \cdot \mathbf{H}_j^{\text{eff}}], \quad (1.8)$$

where $\mathbf{H}_j^{\text{eff}}$ is the effective magnetic field acting on the magnetization \mathbf{M}_j and is given by the formula [42, 17]

$$\mathbf{H}_j^{\text{eff}} = -\frac{\partial \mathcal{H}}{\partial \mathbf{M}_j} + \frac{\partial}{\partial r_\alpha} \frac{\partial \mathcal{H}}{\partial \left(\frac{\partial \mathbf{M}_j}{\partial r_\alpha} \right)}; \quad (1.9)$$

γ_j is the spectroscopic splitting factor (the Landé factor) for magnetic ions of the j th sublattice. Assuming that $\dot{\mathbf{M}}_j = 0$, we can find from (1.8) the equilibrium vectors $\mathbf{M}_j = \mathbf{M}_{j0}$. If we consider only small oscillations of \mathbf{M}_j about its equilibrium value \mathbf{M}_{j0} , the solution of (1.8) can be given in the form

$$\mathbf{M}_j = \mathbf{M}_{j0} + \Delta \mathbf{M}_j,$$

where

$$|\Delta \mathbf{M}_j| \ll |\mathbf{M}_{j0}|. \quad (1.10)$$

After linearization of (1.8) with respect to $\Delta \mathbf{M}_j$, we obtain a system of linear equations which, for samples of sufficiently large dimensions (compared with the wavelength of spin waves) has a plane-wave solution, viz.,

$$\Delta \mathbf{M}_j \sim \exp [i(\omega t - \mathbf{k} \cdot \mathbf{r})], \quad (1.11)$$

where ω is the frequency and \mathbf{k} is the wave vector. The natural frequencies of oscillation of the system (ω) and the dispersion relationships for them, i.e., the form of the functions $\omega = \omega(\mathbf{k})$, may be found from the condition that the determinant of the system of homogeneous equations obtained for the plane-wave amplitude vanishes.

In the quantum-mechanical approach, it is most convenient to use the second quantization method developed for the simplest

ferromagnet by Holstein and Primakoff [43]. For a discrete spin lattice, the most general method was presented by Tyablikov [20]. The method of second quantization is formulated below for the phenomenological theory in the general case of an arbitrary number of magnetic sublattices and an external magnetic field H which is arbitrary in magnitude and direction.

In the quantum-mechanical approach, it is necessary to replace the classical vectors $M_j(\mathbf{r})$ by the corresponding vector operators $\hat{M}_j(\mathbf{r})$, the components of which should satisfy certain transposition rules. These rules may be deduced from the well-known commutation relationships for the components of the vector operator of the total momentum of each magnetic sublattice \hat{J}_j . As is known

$$\hat{J}_{jx}\hat{J}_{jy} - \hat{J}_{jy}\hat{J}_{jx} = i\hat{J}_{jz} \text{ etc.} \quad (1.12)$$

($\hat{J}_{j\alpha}$ are measured in units of \hbar).

Assuming that the total magnetic moment of the j th sublattice is

$$\hat{M}_j = \int \hat{M}_j(\mathbf{r}) d\mathbf{r} = -\mu_j \hat{J}_j, \quad (1.13)$$

where $\mu_j = \gamma_j \hbar$, we find from (1.12) that

$$\hat{M}_{jy}\hat{M}_{jx} - \hat{M}_{jx}\hat{M}_{jy} = i\mu_j \hat{M}_{jz} \text{ etc.}$$

Consequently, according to (1.13),

$$\begin{aligned} \iint [\hat{M}_{jy}(\mathbf{r}) \hat{M}_{jx}(\mathbf{r}') - \hat{M}_{jx}(\mathbf{r}') \hat{M}_{jy}(\mathbf{r})] d\mathbf{r} d\mathbf{r}' = \\ = i\mu_j \iint \hat{M}_{jz}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}'. \end{aligned}$$

The above relationship will be satisfied for any distribution of $\hat{M}_j(\mathbf{r})$ if the integrands are equal. Bearing in mind that the vector operators $\hat{M}_{j\alpha}(\mathbf{r})$ of different sublattices always commute, we finally find that

$$\hat{M}_{jy}(\mathbf{r}) \hat{M}_{j'x}(\mathbf{r}') - \hat{M}_{j'x}(\mathbf{r}') \hat{M}_{jy}(\mathbf{r}) = i\mu_j \hat{M}_{jz}(\mathbf{r}) \delta_{jj'} \delta(\mathbf{r} - \mathbf{r}') \text{ etc.} \quad (1.14)$$

We shall introduce a system of coordinates X_j, Y_j, Z_j for each sublattice j in such a way that the Z_j -axis is parallel to the quantization axis for the corresponding magnetization $M_j(\mathbf{r})$, i.e., the Z_j -axis lies along the equilibrium classical vector M_{j0} . According to Holstein and Primakoff [43], the components of \hat{M}_j in this system of coordinates can be expressed in terms of the second quantization operators $b_r^{(j)}$ and $b_r^{(j)\dagger}$ in the following way:

$$\begin{aligned} \hat{M}_{jx_j} &= \left(\frac{\mu_j M_{j0}}{2} \right)^{1/2} (f_j b_r^{(j)} + b_r^{(j)\dagger} f_j), \quad \hat{M}_{jy_j} = i \left(\frac{\mu_j M_{j0}}{2} \right)^{1/2} (f_j b_r^{(j)} - b_r^{(j)\dagger} f_j), \\ M_{jz_j} &= M_{j0} - \mu_j b_r^{(j)\dagger} b_r^{(j)}, \quad f_j = \left(1 - \frac{\mu_j b_r^{(j)\dagger} b_r^{(j)}}{2M_{j0}} \right)^{1/2}. \end{aligned} \quad (1.15)$$

It is easily confirmed that when conditions of the type (1.14) are satisfied, the operators introduced in this way, b_r and b_r^\dagger , obey the commutation rules of the Bose-Einstein statistics

$$b_r^{(j)\dagger} b_{r'}^{(j')} - b_{r'}^{(j')} b_r^{(j)\dagger} = \delta_{jj'} \delta(\mathbf{r} - \mathbf{r}') \text{ etc.} \quad (1.16)$$

Moreover, the relationships (1.15) in conjunction with (1.16) ensure that the operators $(\hat{M}_j)^2$ are fixed in space, which is one of the initial assumptions of our phenomenological theory:

$$\hat{M}_j^2(\mathbf{r}) = M_{j0} \left(M_{j0} + \frac{\mu_j}{v_j} \right). \quad (1.1')$$

In deducing (1.1') we take into account the fact that, because of the discrete nature of the medium, the right-hand part of (1.16) includes not the exact δ -function [for which $\delta(0) = \infty$], but some "quasi- δ -function" for which $\delta(0) = \frac{1}{v_j}$. Here, v_j is the volume per atom of the j th sublattice.*

The condition of smallness of the oscillations (1.10), can be written in terms of the operators b and b^\dagger as an inequality of the average values

$$\mu_j \langle b_r^{(j)\dagger} b_r^{(j)} \rangle_{\text{av}} \ll M_{j0}. \quad (1.17)$$

In order to express the energy density $\mathcal{H}(\mathbf{r})$ in (1.2) in terms of $b_r^{(j)}$ and $b_r^{(j)\dagger}$, it is necessary to express relationships (1.15), which give these operators in terms of magnetizations $\hat{M}_j(\mathbf{r})$, in a single unified system of coordinates $OXYZ$ coupled to the crystal axes. Transformation from the coordinate system $OXYZ$ to the system $OX_jY_jZ_j$ may be achieved by rotation about axis OY by an angle θ_j , followed by rotation about the axis OZ by an angle φ_j , where θ_j and φ_j are, respectively, the polar and azimuthal angles

*Comparing the relationships (1.1) and (1.1'), we find, as expected from quantum mechanics, that the noncommutative properties of the operators \hat{M}_x , \hat{M}_y and \hat{M}_z cause the length of the vector \hat{M}_j to differ from its maximum projection \hat{M}_{j0} . The relationships (1.1') reduce to the classical relationships (1.1) only when $\mu_0^{(j)} \gg \mu_j$, where $\mu_0^{(j)} = M_{j0} v_j = \mu_j S_j$ is the atomic magnetic moment of the j th sublattice and S_j is its atomic spin.

Thus, we obtain the usual condition for the validity of the classical description of a spin system: $S_j \gg 1$.

of the OZ_j axis in the coordinate system $OXYZ$ (Fig. 1). The projections of the vector M_j in these coordinate systems are related by*

$$\begin{aligned} M_{jx} &= M_{jx_j} \cos \theta_j \cos \varphi_j - M_{jy_j} \sin \varphi_j + M_{jz_j} \sin \theta_j \cos \varphi_j, \\ M_{jy} &= M_{jx_j} \cos \theta_j \sin \varphi_j + M_{jy_j} \cos \varphi_j + M_{jz_j} \sin \theta_j \sin \varphi_j, \\ M_{jz} &= -M_{jx_j} \sin \theta_j + M_{jz_j} \cos \theta_j. \end{aligned} \quad (1.18)$$

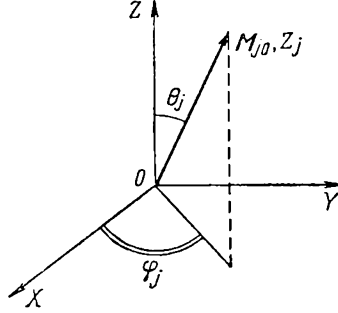


Fig. 1

If instead of the operators $b_r^{(j)}$ and $b_r^{+(j)}$ we now use their Fourier components $b_k^{(j)}$ and $b_k^{+(j)}$:

$$b_r^{(j)} = \frac{1}{V} \sum_k b_k^{(j)} e^{ikr}, \quad b_r^{+(j)} = \frac{1}{V} \sum_k b_k^{+(j)} e^{-ikr}, \quad (1.19)$$

the total Hamiltonian of a magnetic substance (1.3) can be represented, using (1.15), (1.18) and (1.19) in the form of a series of increasing powers of the operators $b_k^{(j)}$ and $b_k^{+(j)}$:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3 + \dots, \quad (1.20)$$

where \mathcal{H}_n is the n th order term with respect to $b_k^{(j)}$ and $b_k^{+(j)}$.

The ground (lowest energy) state of a magnetic system, given by the equilibrium values of the angles $\theta_j = \bar{\theta}_j$ and $\varphi_j = \bar{\varphi}_j$ at $T = 0^\circ\text{K}$, can be found by minimizing with respect to these angles the zeroth-order term \mathcal{H}_0 independent of $b_k^{(j)}$ and $b_k^{+(j)}$. When $\theta_j = \bar{\theta}_j$ and $\varphi_j = \bar{\varphi}_j$, the first-order term \mathcal{H}_1 vanishes. This represents the vanishing of the moment of forces acting on each of the magnetizations M_{j0} at equilibrium. This moment is given by the right-hand part of (1.8).

Thus the ground state of the system can be found either from the minimum of \mathcal{H}_0 or by equating \mathcal{H}_1 to zero.

*We shall omit the superscript " \wedge " over the operator M_j .

The term involving the squares of $b_k^{(j)}$ and $b_k^{(j)\dagger}$ in (1.20), i.e., \mathcal{H}_2 , describes the harmonic oscillations of the magnetizations M_j about their equilibrium positions. In the general case of n sublattices ($j = 1, 2, \dots, n$), this term may be reduced to the following form:

$$\mathcal{H}_2 = \sum_k \mathcal{H}(k),$$

where

$$\begin{aligned} \mathcal{H}(k) = & \alpha_{jj'}(k) (b_k^{(j)} b_k^{(j')} + b_{-k}^{(j)\dagger} b_{-k}^{(j')\dagger}) + \\ & + \frac{1}{2} \beta_{jj'}^*(k) (b_k^{(j)} b_{-k}^{(j')\dagger} + b_{-k}^{(j)\dagger} b_k^{(j')\dagger}) + \frac{1}{2} \beta_{jj'}(k) (b_k^{(j)} b_{-k}^{(j')} + b_{-k}^{(j)} b_k^{(j')}). \end{aligned} \quad (1.21)$$

Here, $\alpha_{jj'}$ and $\beta_{jj'}$ are functions of the wave vector k expressed in terms of the Fourier components of the coefficients A, B, C , etc. in the Hamiltonian (1.2). These functions satisfy the following conditions:

$$\begin{aligned} \alpha_{jj'}(-k) &= \alpha_{jj'}(k), & \beta_{jj'}(-k) &= \beta_{jj'}(k), \\ \alpha_{jj'} &= \alpha_{j'j}^*, & \beta_{jj'} &= \beta_{j'j}. \end{aligned} \quad (1.22)$$

By using linear transformations from operators $b_k^{(j)}$ and $b_k^{(j)\dagger}$ to new Bose-type operators, we can reduce the quadratic form of (1.21) to the diagonal form (cf. Appendix AI). Consequently, \mathcal{H}_2 becomes

$$\mathcal{H}_2 = \Delta \mathcal{H}_0 + \sum_{jk} \varepsilon_{jk} n_{jk}. \quad (1.23)$$

In the above expression, the first term $\Delta \mathcal{H}_0$ is a correction to the ground-state energy \mathcal{H}_0 , due to zero-point vibrations of the system. The second term is the sum of the energies of separate elementary excitations: magnons or spin waves. The function $\varepsilon_{jk} = \varepsilon_j(k)$ gives the dispersion law for the j th mode of spin-wave oscillations (i.e., the form of the dependence of the spin-wave energy on the wave vector k), and n_{jk} is the number of magnons of the j th type with energy $\varepsilon_j(k)$.

The number of spin-wave modes is, in general, equal to the number of magnetic sublattices. However, not all these modes are of equal importance. It can be shown (at least for collinear magnetic structures, cf. Appendix AII) that one mode in the ferromagnetic case and two modes in the antiferromagnetic case are "acoustical" and the remainder are "optical" modes. The "acoustical" modes are those for which there are no energy gaps (disregarding the magnetic anisotropy forces in the absence of a

magnetic field), while all "optical" modes have gaps of the same order of magnitude as the exchange interaction energy of magnetic atoms. If we consider the properties of a magnetic substance under the action of weak external forces (including thermal motion at low temperatures), and the energy of these external forces is small compared with the exchange energies, we can neglect the influence of the optical modes of magnetization oscillation since these modes are not excited.

The acoustical modes of the spin-wave spectrum in a ferromagnetic system represent oscillations of the total magnetic moment of the magnetocrystalline unit cells, and these oscillations do not disturb the collinearity of the component magnetic moments of individual atoms [17]. These oscillations may be excited both by thermal motion and by high-frequency magnetic fields. A constant magnetic field, if small compared with the exchange fields responsible for the magnetic ordering, cannot disturb the collinearity of the magnetic moments of the sublattices in a ferromagnet [20]. Therefore, the properties of a ferromagnet in regard to these weak interactions can always be described by a single effective magnetic sublattice represented by a single local magnetization $M(\mathbf{r})$ and some average magnetomechanical ratio g defined as the quotient of the magnetic and mechanical moments of the magnetocrystalline unit cell (cf. also Chap. XI).

In collinear antiferromagnetic systems, the two acoustical modes of the spectrum represent two degrees of freedom of the antiferromagnetic vector oscillations

$$L = \sum_i^+ M_i - \sum_i^- M_i,$$

where each of the sums is taken over sublattices with the same direction of magnetic moment. However, it is not always possible to describe an antiferromagnet adequately by means of two effective magnetic sublattices (by analogy with ferromagnets). This is true because in antiferromagnets even weak magnetic fields may, in general, disturb the collinearity of initially antiparallel and parallel magnetic moments of the sublattices.

Nevertheless, in many important special cases, antiferromagnets with complex sublattice structures may be described by two local magnetizations $M_1(\mathbf{r})$ and $M_2(\mathbf{r})$. A trivial case of this occurs when all the magnetic sublattices are divided equally into two groups because the exchange interaction between the sublattices within the same group is considerably greater than the interaction between sublattices belonging to different groups. However, we are very interested in another special case, important

in later treatment; viz., the most frequent case of an antiferromagnet in which all the magnetic atoms are crystallochemically equivalent (so that the corresponding lattice sites may always be transposed into self-coincidence by symmetry operations of the space group of the crystal). In this case, at least in weak fields and at low temperatures (which do not destroy the initial antiferromagnetic structure), the collinearity of parallel magnetic moments in the crystallomagnetic unit cell is not disturbed because they are equivalent and are rotated through the same angle. Consequently, an antiferromagnet with any collinear or even weakly noncollinear structure can always be described by means of two sublattices by assigning to one sublattice all the sites having atoms with parallel magnetic moments.

Knowing the energy of spin waves (magnons) and bearing in mind that the distribution of magnons in the states $\varepsilon_j(\mathbf{k})$ under thermodynamic equilibrium conditions is governed by the Bose-Einstein statistics, we can deduce all the thermodynamic properties of a magnetic material: we can find its free energy and determine the temperature dependence of its magnetic susceptibility, magnetization, or spin contribution to its specific heat, etc.

The higher-order terms in the Hamiltonian (1.20), i.e., \mathcal{H}_3 , etc., are similar to the anharmonic terms in the theory of crystal-lattice vibrations, and may be considered as terms representing the processes of collision between quasiparticles (magnons). This makes it possible to carry out consistent quantum-mechanical studies of various relaxation and kinetic processes occurring in magnetic materials [17].

The method described above allows us to determine very simply the natural oscillation frequencies of magnetic moments (the spin-wave spectrum) for two limiting cases: for short waves, when the wavelength λ_k is small compared with the linear dimensions of the sample, L_0 , and for uniform oscillations of M_i throughout the sample, which correspond to infinite wavelengths and, consequently, zero wave vector \mathbf{k} . In many physical problems these two groups of spin waves are of greatest interest. The short spin waves with $\lambda_k \ll L_0$ are usually responsible for various thermal (equilibrium and kinetic) phenomena such as the temperature dependence of the magnetization and specific heat, and the additional electrical resistance and thermal resistance due to scattering on these spin waves, etc. The spin waves with $\mathbf{k} = 0$ are excited at magnetic resonance in a uniform high-frequency magnetic field. Both these cases will be considered later.

CHAPTER II

Ferromagnetism in Uniaxial Crystals

The general method presented in Chap. I was first applied to the simplest magnetic material, the magnetic state of which can be described by a single local magnetization vector $\mathbf{M}(\mathbf{r})$. Such a description may be applied not only to normal ferromagnets but also, under certain conditions, to ferrimagnets with collinear magnetic structure.

In order to use this simplest case for analysis of the role of magnetocrystalline anisotropy forces, we shall consider a uniaxial (trigonal, tetragonal, or hexagonal) crystal. Some of these results are applicable to crystals of other systems.

1. SPIN-WAVE SPECTRUM

The energy density in a ferromagnet, up to terms containing the square of the magnetization $\mathbf{M}(\mathbf{r})$, has the same form for all uniaxial crystals. By considering a uniaxial crystal as a special case of the general expression (1.2) with $n = 1$ we have

$$\begin{aligned} \mathcal{H}(\mathbf{r}) = & A m^2 - K m_z^2 + B_{\perp} \left(\frac{\partial m_x}{\partial x} \frac{\partial m_x}{\partial x} + \frac{\partial m_x}{\partial y} \frac{\partial m_x}{\partial y} \right) + B_z \frac{\partial m_x}{\partial z} \frac{\partial m_x}{\partial z} - \\ & - \frac{1}{2} \mathbf{M}(\mathbf{r}) \nabla \left[\int_V \frac{\text{div } \mathbf{M}(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} - \oint_{\Sigma} \frac{\mathbf{M}(\mathbf{r}') d\mathbf{s}'}{|\mathbf{r} - \mathbf{r}'|} \right] - MH. \end{aligned} \quad (2.1)$$

Here, the first term representing the exchange energy for uniform distribution of the magnetization is constant in view of the condition (1.1) (i.e., $m^2 = \text{const}$), and need not be considered further. The second term gives the magnetocrystalline anisotropy energy, the third and fourth terms give contributions to the exchange energy, and the fifth gives part of the magnetostatic energy.

The third, fourth, and fifth terms are related to perturbations of the uniformity of magnetization. The first integral in the square bracket is taken over the whole volume V of the sample and the second over the whole surface Σ . Finally, the last term represents the energy of the sample in an external magnetic field H . In the Hamiltonian (2.1) we have ignored terms of the type $\frac{\partial m_\alpha}{\partial r_\gamma} \frac{\partial m_\beta}{\partial r_\delta}$, which are anisotropic in m , i.e., dependent on the direction of m with respect to the crystallographic axes. These terms are small, first, because of the low magnetization gradients (this is the condition for applicability of the spin-wave approximation) and second, because of their relativistic origin (cf. Chap. I, Sec. 1).

We can now introduce the Bose operators b_r and b_r^+ , using the relationships (1.15) and assuming that the quantization axis for the magnetization, i.e., the equilibrium direction of the classical magnetization vector M_0 , is the Z' axis. Moreover, in a uniaxial crystal, we can suppose that, in general, the field H lies in the same plane as the axes OZ and OZ' (Fig. 1). By taking this plane to be the XZ plane (and the $X'Z'$ plane) we are automatically assuming that $\varphi_j = \varphi = 0$; the transformation of the system of coordinates (1.18) then reduces to simple rotation by an angle $\theta_j = \theta$ about Y axis.

After use of the Fourier transformation (1.9) and of (1.15)-(1.18) with $\varphi_j = 0$ and $\theta_j = \theta$, the total Hamiltonian of the ferromagnet $\mathcal{H} = \int \mathcal{H}(\mathbf{r}) d\mathbf{r}$, reduces to (1.20). The components of interest to us (the ground-state energy \mathcal{H}_0 and the quadratic term \mathcal{H}_2 , which determine the spin-wave spectrum) now assume the following forms:

$$\frac{\mathcal{H}_0}{V} = \text{const} - K \cos^2 \theta + M_0 H_x \sin \theta - M_0 H_z \cos \theta, \quad (2.2)$$

$$\mathcal{H}_2 = \sum_k \left(\alpha_k b_k^+ b_k + \frac{1}{2} \beta_k b_k^+ b_{-k}^+ + \frac{1}{2} \beta_k^* b_k b_{-k} \right), \quad (2.3)$$

where

$$\begin{aligned} \alpha_k = & \left(1 - \frac{3}{2} \sin^2 \theta \right) \mu H_A + I_k + \mu H_x \sin \theta + \mu H_z \cos \theta + \\ & + 2\pi\mu M_0 \left(\frac{k'_+ k'_-}{k^2} \right) - \left(\frac{4\pi}{3} \right) \mu M_0, \end{aligned} \quad (2.4)$$

$$\beta_k = \frac{1}{2} \mu H_A \sin^2 \theta + 2\pi\mu M_0 \left(\frac{k'_-}{k} \right)^2. \quad (2.4')$$

We use here the notation $H_A = 2K/M_0$, $I_k = (2\mu/M_0) (B_\perp k_\perp^2 + B_z k_z^2)$, $k'_\pm = k_{x'} \pm i k_y = k_x \cos \theta - k_z \sin \theta \pm i k_y$, $k_\perp^2 = k_x^2 + k_y^2$. The last term in α_k is

related to the demagnetizing field of the sample surface (for simplicity, we shall consider a spherical sample).

After reducing \mathcal{H}_2 to the diagonal form (which is easily done by means of the relationships given in Appendix AI) we find that

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_2 = \mathcal{H}_0 + \Delta\mathcal{H}_0 + \sum_k \varepsilon_k n_k, \quad (2.5)$$

where

$$\Delta\mathcal{H}_0 = -\frac{1}{2} \sum_k (\alpha_k - \sqrt{\alpha_k^2 - |\beta_k|^2}) \quad (2.6)$$

is the zero-point energy of spin waves, which gives rise to a correction of the ground-state energy;

$$\varepsilon_k = \sqrt{\alpha_k^2 - |\beta_k|^2} \quad (2.7)$$

is the energy of a spin wave with vector k , and n_k is the number of spin waves in this state.

The following comments must be made about the zero-point oscillation energy $\Delta\mathcal{H}_0$ and the limits of applicability of the above expressions for the energy spectrum.

If we study the continuous medium model rigorously using the energy density in the expression (2.1), then, because the operators b_r and b_r^+ are noncommutative, in addition to terms in $\Delta\mathcal{H}_0$ we also have zero-point energy terms in \mathcal{H}_0 itself because in the initial quadratic form $\mathcal{H}_2(r)$ we have eliminated terms of the type $b_r b_r^+$ by means of the commutation relations (1.16). These terms are unimportant in the exchange part of the energy since they are independent of the angle θ and the field H , and they can be simply included in the additive constant \mathcal{H}_0 . At the same time, the anisotropy energy, $-Km_z^2(r)$ in (2.1), allowing for the noncommutative nature of b_r and b_r^+ , makes a contribution to \mathcal{H}_0 which depends on the angle θ . In place of the second term in \mathcal{H}_0 in (2.2), we obtain an expression which differs from it by the replacement of K with $K_q = K \left(1 - \frac{1}{M_0 v}\right) = K \left(1 - \frac{1}{2S}\right)$. Here again we have made use of the quasicontinuity of the medium, assuming that $\delta(r)|_{r=0} = \frac{1}{v}$ (in a true continuous medium with an infinite number of degrees of freedom the zero-point energy becomes infinite). The quantum correction is particularly important when the atomic spin is $S = 1/2$, since in this case the energy of the type Km_z^2 has no anisotropy at all.

The main difficulty in making quantum corrections is as follows. Strictly speaking, the noncommutative nature of operators b_r and b_r^+ invalidates the rejection of higher-order terms of these operators ($\mathcal{H}_3, \mathcal{H}_4$, etc.) in the total Hamiltonian (1.20) compared with the terms $\mathcal{H}_0, \mathcal{H}_1, \mathcal{H}_2$, so that the expansion indicated in (1.20) is, in fact, in terms of the parameter $1/S$, which, with the exception of the classical case $S \gg 1$, is hardly small. Thus, at first sight, it seems that the expressions given above for \mathcal{H}_0 in (2.2) and \mathcal{H}_2 in (2.3) are applicable only in the classical limit. However, their validity is, in fact, broader. To show this, we write the magnetic anisotropy energy of a uniaxial crystal in a more general form:

$$\mathcal{H}_{\text{anis}} = - \int K(\mathbf{r} - \mathbf{r}') m_z(\mathbf{r}) m_z(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (2.8)$$

which allows for the correlation of magnetic moments at various points in a crystal. (Obviously, we can write the exchange energy in the same way, cf. Appendix B.)

In the above calculation we have used the special form of the expression (2.8) with $K(\mathbf{r} - \mathbf{r}') = K\delta(\mathbf{r} - \mathbf{r}')$, which allows only for the intrinsic local anisotropy energy at each lattice site. In that case, the noncommutative nature of operators b_r and b_r^+ leads to the difficulties mentioned above in allowing for the zero-point energy. However, the other possibility is that the anisotropy energy plays the main role when it is related to the correlation of magnetic moments at different lattice sites, so that we can assume that

$$K(\mathbf{r} - \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} = 0.$$

If this correlation exists over short distances only (in a "magnetic anisotropy volume" [44]) the expression (2.8) can be expressed in the form

$$\mathcal{H}_{\text{anis}} = -K \int m_z(\mathbf{r}) m_z(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} d\mathbf{r} + \text{terms with gradients } m_z(\mathbf{r}), \quad (2.8')$$

which are not included because of their smallness (see the beginning of the present section); here, $K = \int K(\mathbf{r}' - \mathbf{r}) d\mathbf{r}'$ is a constant which is independent of the choice of coordinates. The anisotropy energy density, given by the expression (2.8'), is only formally identical with the corresponding term in the Hamiltonian (2.1). The difference is that the operators b_r and b_r^+ should commute if they appear with different multipliers in (2.8'). Consequently, we may assume that $b_r b_r^+ = b_r^+ b_r$ for the corresponding term in \mathcal{H}_2 .

It is easily shown that this treatment of the origin of the anisotropy energy in the initial Hamiltonian (2.1) yields for \mathcal{H}_0 and \mathcal{H}_2 expressions given by the formulas (2.2) and (2.3).

Thus, the above formulas and all the results which follow from them are valid in two cases:

- 1) in the case of a local origin of the magnetic anisotropy, if $S \gg 1$, and
- 2) in the case of a correlated nature of the magnetic anisotropy for any value of S including $S = 1/2$.

A more detailed calculation of the energy spectrum and an estimate of the quantum correction $\Delta\mathcal{H}_0$ to the ground-state energy \mathcal{H}_0 are given for the second case in Appendix B.

The equilibrium value of angle θ , which occurs in the expression for the spin-wave energy (2.7), is found from the minimum value of \mathcal{H}_0 . If we represent by ψ the angle between the external field H and the Z symmetry axis, the condition for a minimum of \mathcal{H}_0 gives, in general, the following expression for the determination of θ :

$$H_A \sin 2\theta = 2H \sin(\psi - \theta). \quad (2.9)$$

We shall now consider in greater detail two special cases of the field direction: $H \parallel Z$ and $H \perp Z$.

1. $H \parallel Z$. In this case $\psi = 0$, and the expression (2.9) has the following two solutions:

$$1) \sin \theta = 0, \quad 2) \cos \theta = -\frac{H}{H_A}. \quad (2.10)$$

The first of these solutions corresponds to an energy minimum for any value of the field H and a positive anisotropy constant $K > 0$ (when the symmetry axis Z is the easy magnetization axis) as well as for $K < 0$ (when Z is the hard magnetization axis) in fields $H \geq H_A$. The second solution is obtained for $K < 0$ when $H \leq H_A$: with increase in H , the magnetic moment is gradually rotated from the basal plane toward the Z axis; when $H = |H_A|$, it becomes parallel to this axis, which represents saturation.

The spin-wave energies corresponding to the solutions of (2.10) have the following form, according to expressions (2.7), (2.4), and (2.6):

$$1) \varepsilon_k = \left\{ \left[I_k + \mu \left(H + H_A - \frac{4\pi}{3} M_0 \right) \right] \left[I_k + \mu \left(H + H_A - \frac{4\pi}{3} M_0 \right) + 4\pi\mu M_0 \frac{k_x^2 + k_y^2}{k^2} \right] \right\}^{1/4}, \quad (2.11)$$

$$\begin{aligned}
2) \quad \varepsilon_k = & \left\{ \left(I_k - \frac{4\pi}{3} \mu M_0 \right) \left[I_k - \mu H_A \left(1 - \frac{H^2}{H_A^2} \right) - \right. \right. \\
& \left. \left. - \frac{4\pi}{3} M_0 + 4\pi \mu M_0 \frac{k_x'^2 + k_y'^2}{k^2} \right] - \mu H_A \left(1 - \frac{H^2}{H_A^2} \right) 4\pi \mu M_0 \frac{k_x'^2}{k^2} \right\}^{1/2}, \quad (2.12) \\
& \left(k_x' = -k_x \frac{H}{H_A} - k_z \sqrt{1 - \left(\frac{H}{H_A} \right)^2} \right).
\end{aligned}$$

Expression (2.11) is practically identical with the corresponding results of Holstein and Primakoff [43] and of Herring and Kittel [16], who have discussed precisely this case.*

2. $H \perp Z$. When $\psi = \pi/2$ the expression (2.9) has two other solutions:

$$1) \cos \theta = 0, \quad 2) \sin \theta = \frac{H}{H_A}. \quad (2.13)$$

If $K > 0$ the second solution applies in the range of fields from 0 to H_A , while the first solution is valid for $H \geq H_A$. If $K < 0$, the first solution is obtained for any value of H . The corresponding spin-wave energies can be written in the following form

$$\begin{aligned}
1) \quad \varepsilon_k = & \left\{ \left[I_k + \mu \left(H - \frac{4\pi}{3} M_0 \right) \right] \left[I_k + \mu \left(H - H_A - \frac{4\pi}{3} M_0 \right) + \right. \right. \\
& \left. \left. + 4\pi \mu M_0 \frac{k_y^2 + k_z^2}{k^2} \right] - \mu H_A \cdot 4\pi \mu M_0 \frac{k_z^2}{k^2} \right\}^{1/2}, \quad (2.14)
\end{aligned}$$

$$\begin{aligned}
2) \quad \varepsilon_k = & \left\{ \left[I_k + \mu \left(H_A - \frac{4\pi}{3} M_0 \right) \right] \left[I_k + \mu H_A \left(1 - \frac{H^2}{H_A^2} \right) - \frac{4\pi}{3} \mu M_0 + \right. \right. \\
& \left. \left. + 4\pi \mu M_0 \frac{k_x'^2 + k_y'^2}{k^2} \right] - \mu \frac{H^2}{H_A} 4\pi \mu M_0 \frac{k_x'^2}{k^2} \right\}^{1/2}, \quad (2.15) \\
& \left(k_x' = k_x \sqrt{1 - \frac{H^2}{H_A^2}} - k_z \frac{H}{H_A} \right).
\end{aligned}$$

We note that the general expression (2.7), with the values of α_k and β_k defined by formulas (2.4) and (2.4'), and the special cases (2.11), (2.12), (2.14), and (2.15), determine the energy of short spin waves with wavelength $\lambda_k \ll R$, where R is the radius of the spherical sample. From this expression we cannot obtain directly (as the limiting case at $k = 0$) the spectrum of uniform spin oscillations excited at resonance in a uniform high-frequency magnetic field.

*In the cited work [16, 43] the demagnetizing field $-\frac{4\pi}{3} M_0$ was neglected because the authors considered an infinitely long sample along the Z axis.

In general, the frequencies of uniform magnetic resonance have to be determined separately, starting again from the Hamiltonian (2.1) and taking into account the uniformity of the vector $\mathbf{M}(\mathbf{r})$ (the independence of coordinates over the whole volume of the sample). In the case of spherical samples, this leads to expressions that can be obtained from corresponding expressions for short spin waves by rejecting all the terms which depend on the wave vector \mathbf{k} and all the terms of the type $-\frac{4\pi}{3}M_0$ due to the demagnetizing effect of the sample surface.*

We shall now write the expressions for the resonance frequencies $\omega_0 = \varepsilon_0/\hbar$ for $K > 0$ and $K < 0$ respectively

For $K > 0$:

$$\text{a) } \mathbf{H} \parallel \mathbf{Z}, \quad \omega_0 = \gamma (H + H_A); \quad (2.16)$$

$$\text{b) } \mathbf{H} \perp \mathbf{Z}, \quad \omega_0 = \gamma \sqrt{H_A^2 - H^2} \text{ for } H \leq H_A; \quad (2.17)$$

$$\omega_0 = \gamma \sqrt{H(H - H_A)} \text{ for } H \geq H_A. \quad (2.18)$$

For $K < 0$:

$$\text{c) } \mathbf{H} \parallel \mathbf{Z}, \quad \omega_0 = 0 \text{ for } H \leq |H_A|; \quad (2.19)$$

$$\omega_0 = \gamma (H - |H_A|) \text{ for } H \geq |H_A|; \quad (2.20)$$

$$\text{d) } \mathbf{H} \perp \mathbf{Z}, \quad \omega_0 = \gamma \sqrt{H(H + |H_A|)}. \quad (2.21)$$

The dependence of the resonance frequency on the magnetizing field, expressed by formulas (2.16)-(2.21) above, is shown schematically in Fig. 2.

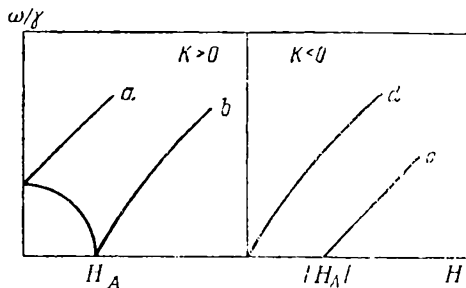


Fig. 2

*The latter is due to the fact that for a sphere the demagnetizing field energy under uniform magnetization conditions is $\frac{1}{2} \frac{4\pi}{3} (M_x^2 + M_y^2 + M_z^2)$ and, therefore, does not affect the oscillation frequency.

The lack of an energy gap in the excitation of spin waves in the (2.19) case is due to the degeneracy of uniaxial ferromagnets with respect to the azimuthal angle φ of the magnetization vector. This degeneracy is removed by allowing for the higher-order anisotropy terms in the Hamiltonian (fourth-order for tetragonal crystals, and sixth-order for hexagonal).

We note that formulas (2.16)-(2.21) apply to the resonance frequency at $T = 0^\circ \text{K}$. However, it is easily understood that they are of the same form at any finite temperature T if H_A is taken to be the anisotropy field corresponding to this temperature.*

2. SPONTANEOUS MAGNETIZATION AND INTRINSIC SUSCEPTIBILITY OF A FERROMAGNET

Before considering particular problems, we shall begin by calculating the dependence of the magnetization of a ferromagnet on temperature and the external field under magnetic saturation conditions. Saturation is understood to be a single-domain state of a ferromagnet such that the magnetization throughout the sample is parallel to the magnetizing field. To reach saturation, it is necessary in general to apply a sufficiently strong magnetic field, i.e., a field greater than the demagnetizing fields and the magnetic anisotropy field. The saturation magnetization $M = M(T, H)$ measured under these conditions is then sometimes identified with the spontaneous magnetization $M_s = M_s(T)$, i.e., with the magnetization which would be obtained by extrapolating M to $H = 0$. This neglects the intrinsic magnetization due to the partial suppression of spin waves by the magnetic field itself. The aim of the present section is to consider, in greater detail than usual, the role of this intrinsic magnetization.

The intrinsic susceptibility was calculated by Holstein and Primakoff [43]. However, because they allowed for the magneto-static (dipole-dipole) energy, their calculations and results are very cumbersome. Moreover, they did not clearly define the limits of applicability of their results. We shall consider one important special case for which

$$H \gg 4\pi M_0, \quad |H_A| \quad (2.22)$$

*Thus in formulas (2.16)-(2.21) it is necessary to make the substitution

$$H_A \rightarrow H_A(T) = \frac{2K(T)}{M(T)},$$

where $K(T)$ and $M(T)$ are, respectively, the anisotropy constant and the saturation magnetization at temperature T .

so that we can neglect both the magnetostatic energy and the anisotropy energy. In this case, the spin-wave energy has the well-known "Bloch" form:*

$$\varepsilon_k = Ik^2 + \mu H; \quad \left(I = \frac{2\mu}{M_0} B \right). \quad (2.23)$$

We shall first write the general relationships for calculating the magnetization of the system whose energy spectrum is given by the expression (2.5). The thermodynamic potential of the system can be represented in the form

$$\Omega = \mathcal{H}_0 + \Delta \mathcal{H}_0 + \kappa T \sum_k \ln (1 - e^{-\varepsilon_k/\kappa T}). \quad (2.24)$$

The average magnetization in the direction α ($\alpha = X, Y, Z$) is given by the relationships

$$M_\alpha(T, H) = - \frac{1}{V} \frac{\partial \Omega}{\partial H_\alpha} = M_\alpha(0, H) - \Delta M_\alpha(T, H), \quad (2.25)$$

$$M_\alpha(0, H) = - \frac{1}{V} \frac{\partial}{\partial H_\alpha} (\mathcal{H}_0 + \Delta \mathcal{H}_0), \quad (2.26)$$

$$\Delta M_\alpha(T, H) = \frac{1}{V} \sum_k \frac{\partial \varepsilon_k}{\partial H_\alpha} \bar{n}_k, \quad (2.27)$$

where

$$\bar{n}_k = (e^{\varepsilon_k/\kappa T} - 1)^{-1} \quad (2.28)$$

is the Bose distribution function for spin waves.

In the case of strong fields, as defined by (2.22), the saturation magnetization at $T = 0^\circ \text{K}$ is**

$$M(0, H) \simeq M_0. \quad (2.29)$$

*The results given below apply to crystals of any system, and therefore in (2.23) we shall not allow for the anisotropy of B , bearing in mind that if this anisotropy does exist, in the final result B will simply be replaced by some effective value (cf. Sec. 3 in Chap. II).

**In general, the energy of zero-point oscillations leads to a dependence of M on the field even at absolute zero. For example in the case of magnetization along the easy axis with the condition given by (2.22), instead of (2.29), Holstein and Primakoff obtained a more exact expression of the type

$$M = M_0 - \frac{M}{2} \left(\frac{2\pi\mu M_0}{I} \right)^{3/4} \left(\frac{2\pi M_0}{H} \right)^{1/4}. \quad (2.29')$$

However, the field-dependent second term in the above expression when (2.22) is satisfied at not too low temperature, so that $\kappa T \gg 2\pi\mu M_0$ is always small compared with the field-dependent magnetization related to thermal motion [cf. formulas (2.29') and (2.35)].

The dependence of the saturation magnetization on temperature and field is, according to formulas (2.27) and (2.23), given by

$$\Delta M (T, H) = \frac{\mu}{V} \sum_k \bar{n}_k,$$

which, after integration, becomes

$$\Delta M (T, H) = \frac{\mu \Gamma (3/2)}{4\pi^2} \left(\frac{\chi T}{I} \right)^{3/2} F_{3/2} (h), \quad (2.30)$$

where $h = \mu H / \chi T$. The function $F_{3/2} (h)$ is the integral

$$F_{\sigma} (h) = \frac{1}{\Gamma (\sigma)} \int_0^{\infty} \frac{x^{\sigma-1}}{e^{x+h} - 1} dx \quad (2.31)$$

for $\sigma = \frac{3}{2}$.

Integrals of the above type have been investigated and tabulated by Robinson and Clunie [45], so that the functional dependence $\Delta M (T, H)$ can be represented graphically in general form with the required precision. The function $F_{\sigma} (h)$ can also be represented as a series in powers of h :

$$F_{\sigma} (h) = \Gamma (1 - \sigma) h^{\sigma-1} + \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \zeta (\sigma - n) h^n, \quad (2.32)$$

where $\zeta (x)$ is the Riemann function and $\Gamma (x)$ is the gamma function.* In particular:

$$F_{3/2} (h) = \zeta (3/2) (1 - 1.36 h^{1/2} + 0.56 h - 0.04 h^2 + 0.0016 h^3 - \dots). \quad (2.33)$$

This expression makes it possible to distinguish the spontaneous magnetization at a temperature T , obtained by extrapolation to $H = 0$ [the extrapolation is given by the formula (2.33)], and the intrinsic magnetization, given by the difference

$$F_{3/2} (h) - F_{3/2} (0).$$

*The following property of the function $F_{\sigma} (h)$ is also very useful:

$$\frac{\partial^n F_{\sigma} (h)}{\partial h^n} = (-1)^n F_{\sigma-n} (h).$$

Now, let us assume that

$$\kappa T \gg \mu H, \text{ i.e. } h \ll 1. \quad (2.34)$$

Instead of (2.30), we can then write approximately

$$\Delta M(T, H) = 0,06 \mu \left(\frac{\kappa T}{I} \right)^{3/2} \left[1 - 1,36 \left(\frac{\mu H}{\kappa T} \right)^{1/2} \right]. \quad (2.35)$$

For example, if $H = 10^4$ oersteds and $T = 10^\circ \text{ K}$ ($h \sim 0.1$), the second term in (2.35) is more than 40% of the first term. Thus, even if the condition (2.34) is satisfied, the intrinsic magnetization may strongly affect the temperature dependence of the saturation magnetization.

It is usual to describe the intrinsic magnetization phenomenon by the intrinsic susceptibility $\chi_p = \frac{\partial}{\partial H} M(T, H)$. The following general expression can be obtained for this susceptibility:

$$\chi_p = \frac{\mu^2 \Gamma(3/2)}{4\pi^2 \kappa T} \left(\frac{\kappa T}{I} \right)^{3/2} F_{1/2}(h). \quad (2.36)$$

When the condition (2.34) is satisfied, we obtain a simpler relationship

$$\chi_p = 2,68 \cdot 10^{-18} \left(\frac{\mu}{I} \right)^{3/2} \frac{T}{V H}. \quad (2.37)$$

The above relationship, which shows that the intrinsic susceptibility is directly proportional to $H^{-1/2}$, has been confirmed experimentally by Rode and Gofman [46] for ferromagnetic nickel-copper alloys.

In the opinion of this author, precision measurements of χ_p as a function of temperature and field can be used as a further independent method of experimentally determining the exchange coupling parameter I . The best conditions for these measurements are realized in single-crystal samples magnetized along the easy axis. It is important to note that the parameter I can be found not only from the curve $\chi_p = \chi_p(T)$, recorded for constant H , but also from the curve $\chi_p = \chi_p(H)$, recorded at constant T .

3. MAGNETIZATION CURVE ALONG THE HARD DIRECTION

The second example of the application of the energy spectrum obtained earlier is the temperature dependence of the magnetization curve of a uniaxial single-domain ferromagnet along the

hard magnetization axes. In other words, we shall find the function

$$M_H = M_x(T, H) \text{ when } K > 0 \text{ or } M_H = M_z(T, H) \text{ when } K < 0.$$

We shall now consider a region of not too low temperatures, such that

$$\kappa T \gg \mu H, \mu H_A, 4\pi\mu M_0. \quad (2.38)$$

Under these conditions, a calculation using the formulas (2.25)-(2.27) gives the following general result for the two cases of interest to us:

$$M_H \simeq M_0 \frac{H}{H_A} \left(1 - \frac{\mu}{M_0 V} \sum_k \bar{n}_k \right) \text{ when } H \leq H_A, \quad (2.39)$$

$$M_H \simeq M_0 \left(1 - \frac{\mu}{M_0 V} \sum_k \bar{n}_k \right) \text{ when } H \geq H_A. \quad (2.40)$$

Here, $\sum \bar{n}_k$ is the total number of spin waves at a temperature T , which, if intrinsic magnetization is neglected, is given by the following relationship, provided the condition (2.38) is satisfied:

$$\frac{1}{V} \sum \bar{n}_k \simeq 0,06 \frac{(\kappa T)^{3/2}}{I_{\perp} \sqrt{I_z}}, \quad (2.41)$$

where $I_{\perp z} = \frac{2\mu}{M_0} B_{\perp, z}$.

It is easily seen that the formula (2.39) leads to $M_H > M_0$ for H sufficiently close to H_A , and this contradicts one of the initial assumptions of the theory, given by the expression (1.1). Moreover, the magnetization is supposed to change discontinuously at $H = H_A$, which also has no physical meaning. These difficulties are only apparent. The fact is that the quantity H_A represents the saturation field at absolute zero. In order to find the magnitude of the saturation field at a finite temperature T , it is necessary to calculate how the equilibrium direction of the average magnetization vector, i.e., the angle θ , varies as a function of H at this temperature.*

This can be done using the condition for a minimum of the thermodynamic potential Ω , given in the formula (2.24), by varying the latter with respect to the angle θ . Then, for \mathcal{H}_0 and ε_k we should obviously use the general expressions (2.2) and (2.7), taking into

*At absolute zero, the angle θ is given by the formulas (2.10) or (2.13).

account (2.4) which gives the dependence of these quantities on θ . Consequently, in place of (2.10) and (2.13), we obtain relationships of the following type:

when $K > 0$, $H \perp Z$

$$\sin \theta = \frac{H}{H_A^T} \text{ when } H \leq H_A^T \text{ and } \sin \theta = 1 \text{ when } H \geq H_A^T; \quad (2.42)$$

when $K < 0$, $H \parallel Z$

$$\cos \theta = \frac{H}{|H_A^T|} \text{ when } H \leq |H_A^T| \text{ and } \cos \theta = 1 \text{ when } H \geq H_A^T, \quad (2.43)$$

where

$$H_A^T = H_A \left(1 - 2 \frac{\mu}{M_0 V} \sum_k \bar{n}_k \right). \quad (2.44)$$

Thus, the magnetic field at which magnetic saturation is reached, i.e., at which the magnetization becomes parallel to the magnetizing field, depends on the temperature, decreasing as the latter increases. The formulas (2.39) and (2.40) for the temperature dependence remain fully valid; one must remember, however, that the limit of applicability of these formulas is now at $H = H_A$ and not at $H = H_A^T$. Using H_A^T , these formulas can now be simplified:

$$M_H = M \frac{H}{H_A^T} \quad \text{when } H \leq H_A^T \quad (2.45)$$

and

$$M_H = M \quad \text{when } H \geq H_A^T, \quad (2.46)$$

where

$$M = M_0 \left(1 - \frac{\mu}{M_0 V} \sum \bar{n}_k \right) \quad (2.47)$$

is the saturation magnetization at a given temperature T .* Figure 3 shows schematically the magnetization curves along the hard direction for $T = 0^\circ\text{K}$ and $T > 0^\circ\text{K}$.

*It is easily seen that the saturation field $H = H_A^T$ at this temperature can also be found from the condition of equality of the right-hand parts of formulas (2.39) and (2.40).

We note that the formula (2.44) determines, in fact, the temperature dependence of the anisotropy constant, since it can be rewritten as follows:

$$K(T) = K(0) \left(1 - 3 \frac{\mu}{M_0 V} \Sigma \bar{n}_k \right), \quad (2.48)$$

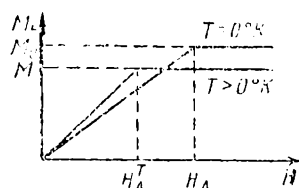


Fig. 3

where $K(T) = 1/2 MH_A^T$ and $K(0) \equiv K$. Using formula (2.47), the temperature change of the anisotropy constant $\Delta K(T) = K(0) - K(T)$ can be expressed in terms of the change of the saturation magnetization $\Delta M = M(0) - M(T)$:

$$\frac{\Delta K(T)}{K(0)} = 3 \frac{\Delta M(T)}{M(0)}. \quad (2.49)$$

Using the condition $\Delta M(T) \ll M(0)$, the above relationship can be written in the form

$$\frac{K(T)}{K(0)} = \left[\frac{M(T)}{M(0)} \right]^3, \quad (2.50)$$

which was found to be in agreement with the well-known Akulov-Zener law [47, 48] (cf. Chap. III).

We would stress once again that these simple relationships for the temperature dependence of the magnetization and the anisotropy constant are valid only at not too low temperatures, the range being defined by the condition (2.38). Since H_A and $4\pi M_0$ usually lie within the range 10^3 - 10^4 oersted, this temperature range extends down to 0.1-1.0°K. It is interesting that when the condition (2.38) is satisfied, the magnetostatic energy of a ferromagnet has little influence on its thermodynamic properties. This result has been obtained for the saturation magnetization $M(T, H)$ by Holstein and Primakoff [43].* The temperature dependence of M for other possible limiting cases was calculated by Kaganov and Tsukernik [49, 17].

4. TEMPERATURE DEPENDENCE OF THE MAGNETIZATION OF DYSPROSIUM

We shall consider one more special case, different from (2.38), which is also realized in practice. Let the anisotropy constant

*Nevertheless, Holstein and Primakoff showed [43] that the magnetostatic energy might be important in the intrinsic susceptibility of a ferromagnet when condition (2.22) is not satisfied.

K be negative and so large that in the temperature region considered

$$4\pi\mu M_0 \ll \kappa T \ll \mu |H_A|. \quad (2.51)$$

We shall find the temperature dependence of the spontaneous magnetization for this case. Since the easy magnetization axis lies in the basal plane, it is necessary to use the expression (2.14) for the spin-wave energy in calculating $\Delta M_s(T)$. From that expression it is easy to obtain, using (2.51)

$$\left. \frac{\partial \varepsilon_k}{\partial H} \right|_{H=0} \simeq \mu \frac{|H_A|}{2\varepsilon_k} \quad (2.52)$$

and

$$\varepsilon_k|_{H=0} \simeq |I_k \mu |H_A|. \quad (2.53)$$

Since $I_k \propto k^2$, the dispersion law for ε_k is, in this case, linear and not quadratic. Consequently, using the relationships (2.27), we find that

$$\Delta M_s(T) = \frac{1}{24} \mu \sqrt{\frac{I_z}{\mu |H_A|} \frac{(\kappa T)^2}{I_z I_z}}. \quad (2.54)$$

The thermally induced change in the spontaneous magnetization is proportional to T^2 in some rare-earth transition metals: dysprosium, erbium, and holmium [50]. In the ferromagnetic region these metals have negative and very high anisotropy constants. For example, the value of K for dysprosium is of the order of 10^8 erg/cm³, so that $\mu |H_A| \sim 10^2$ °K. Since dysprosium is ferromagnetic below 85°K, we are dealing with the case considered above.

The magnetization of dysprosium along the hexagonal axis increases linearly with the field H up to the strongest fields used in practice ($\approx 10^4$ oersteds). It is interesting to calculate the temperature dependence of the magnetic susceptibility along the hexagonal axis. The spin-wave energy for this direction ($K < 0$, $H \parallel Z$) is given by (2.12) from which, with the condition (2.51) obeyed, we find

$$\frac{\partial \varepsilon_k}{\partial H} \simeq -\mu \frac{\varepsilon_k}{[\mu H_A]} \frac{H}{|H_A|} \quad (2.55)$$

and again

$$\varepsilon_k \simeq |I_k| \mu |H_A|.$$

The variation of the magnetic susceptibility with temperature, determined using the formula (2.27), is

$$\Delta\chi_z = \frac{\Delta M_z}{H} = -\frac{\pi^2}{30} \frac{\mu}{|H_A|} \left(\frac{I_z}{\mu |H_A|} \right)^{1/2} \frac{(\kappa T)^4}{I_{\perp} I_z (\mu H_A)^2}. \quad (2.56)$$

Thus, the susceptibility of dysprosium (or any similar ferromagnet) along its crystal axis should increase with temperature as T^4 . It would be desirable to check this experimentally.

It is easily shown that the spin-wave contribution to the specific heat of a ferromagnet C_s is, because of the linearity of the dispersion law for spin waves, proportional to T^3 , like the phonon specific heat but unlike the normal ferromagnets for which $C_s \propto T^{3/2}$ [17]. We can deduce the following relationship for all three quantities considered, M_s , χ_z and C_s .

$$\frac{C_s}{T\chi_z} = \frac{16\pi^2}{5} \left(\frac{\kappa}{\mu} \right)^2 \frac{M_s(0) - M_s(T)}{M_s(0)}.$$

In conclusion, we note that the existence of the zero-point energy of spin waves, (2.6), contributes, in general, a correction to the ground-state energy of a ferromagnet and, consequently, to its magnetization at $T = 0^\circ\text{K}$. The appearance of a value of $\Delta\mathcal{H}_0$ of nonvanishing magnitude is due to the magnetostatic interaction, and also to the magnetic anisotropy energy. As shown by Holstein and Primakoff [43] and mentioned above (see the first footnote in Chap. II, Sec. 2), the magnetostatic energy gives through $\Delta\mathcal{H}_0$ a correction to the magnetization which is small compared not only with M_0 but also with $\Delta M(T, H)$ if $4\pi\mu M_0 \ll \kappa T$.

Similarly, we can show [40] that the energy $\Delta\mathcal{H}_0$ of the zero-point oscillations arising from the magnetocrystalline anisotropy forces gives a correction to the magnetization, the relative value of which (compared with the magnetization due to \mathcal{H}_0) represents in the most favorable case a quantity of the order of H_A/H_E , where $H_E = 1/\mu a^2 \sim \kappa\Theta_c/\mu$ is the effective exchange field and a is the interatomic spacing (cf. Appendix B). Since usually $H_A/H_E \sim 10^{-4}$ - 10^{-2} , this correction is, as a rule, small. It is also small compared with the temperature variation of the magnetization if $\kappa T \gg \mu |H_A|$. Moreover, as already pointed out above, the quantum corrections are unimportant in the limiting classical case for large atomic spins $S \gg 1$. We may assume that the latter case is realized in dysprosium for which $S = 5$.

CHAPTER III

Temperature Dependence of the Magnetocrystalline Anisotropy and of the Magnetostriiction of Ferromagnets

The temperature dependence of the spontaneous magnetization of a ferromagnet is one of the criteria used to check the hypothesis of the exchange (spin) nature of ferromagnetism. Correspondingly, the temperature dependence of the magnetic anisotropy constants and of the magnetostriiction may be of decisive importance in checking our basic ideas on the nature of those intrinsic magnetic phenomena in ferromagnets which are assumed to be due to relativistic forces.

Akulov [47] and Zener [48] developed a classical theory of the temperature dependence of the magnetic anisotropy constants which did not specify the nature of the forces causing the anisotropy. They started from the assumption that in a crystal we can distinguish short-range order regions of the magnetic moments around each atom in which the local anisotropy constants are independent of temperature. The directions of the local instantaneous magnetizations of these regions are, due to thermal motion, distributed at random, and this determines the resultant average magnetization of the whole crystal. By averaging the phenomenological expressions for the local anisotropy energy over all possible orientations of the magnetization of these regions, it is possible to obtain an expression for the average (free) energy of a crystal in which the local magnetizations and anisotropy constants are replaced by corresponding average macroscopic values. The macroscopic constants of the N th order are then related to the average magnetization of the crystal at a temperature T by the following expression:

$$\frac{K_N(T)}{K_N(0)} = \left[\frac{M(T)}{M(0)} \right]^{N(2N+1)} \quad (3.1)$$

The order N of the anisotropy constant K_N is a number equal to half the power of the invariant, consisting of the components of M , which is associated with K_N (the anisotropy energy should consist only of the even powers of the magnetization). In formula (3.1), $K_N(T)$ and $K_N(0)$ are the anisotropy constants, and $M(T)$ and $M(0)$ are the magnetizations at temperature T and at absolute zero, respectively. An important assumption of the theory is that $K_N(0)$ and $M(0)$ are regarded as the local values of the anisotropy constant and the modulus of the magnetization.

In many papers the temperature dependence of the anisotropy constants is considered on the basis of various special models. Carr [56] has shown that the same result (3.1) can, in fact, be obtained in the molecular field approximation. Tyablikov and Gusev [51], Pal [52], Keffer [53], Kasya [54], Potapkov [55], and others have considered this problem using the microscopic theory of spin waves. The results of these workers for the first ($N = 1$) and second ($N = 2$) anisotropy constants of uniaxial and cubic crystals are in approximate agreement with the formula (3.1), which predicts $K_1 \propto M^3$ and $K_2 \propto M^{10}$. Experiments, however, do not confirm this simple and universal temperature dependence of the anisotropy constants. For example, the constant K_2 of various cubic ferrites varies much less rapidly with temperature than required by the M^{10} law. For a long time it has been assumed that the proportionality of K_2 to the tenth power of the magnetization was satisfied by iron. However, the latest experimental work [57] has yielded a different result: $K_2 \propto M^4$ or $K_2 \propto M^5$. On the other hand, the value of K_2 for nickel rises much faster on cooling than is predicted by the M^{10} law. Consequently, it is necessary to calculate the temperature dependence of the magnetocrystalline anisotropy constants of ferromagnets at low temperatures using the phenomenological theory of spin waves, and taking as a basis only the symmetry considerations and the basic concepts of the nature of ferromagnetism and magnetic anisotropy. The present chapter deals mainly with this problem.

We shall also consider the temperature dependence of the magnetic anisotropy related to magnetostriction and the temperature dependence of the magnetostrictive deformations of ferromagnetic crystals.

1. SPIN-WAVE SPECTRUM AND FREE ENERGY OF THE MAGNETIC ANISOTROPY

The phenomenological Hamiltonian of an anisotropic ferromagnet is, in its general form,*

*We have not allowed for the magnetostatic energy since we shall consider the temperature range $kT \gg 4\pi\mu M_0$, in which this energy is unimportant.

$$\mathcal{H} = \int \mathcal{H}(\mathbf{r}) d\mathbf{r}, \quad (3.2)$$

$$\mathcal{H}(\mathbf{r}) = B_{\beta\delta} \frac{\partial m_\alpha}{\partial r_\beta} \frac{\partial m_\alpha}{\partial r_\delta} + K_{n_1 n_2 n_3} m_x^{n_1} m_y^{n_2} m_z^{n_3} - M_0(\mathbf{m}H). \quad (3.3)$$

Here, $\alpha, \beta, \dots = x, y, z$; n_1, n_2, n_3 are integers such that $n_1 + n_2 + n_3 = 2N$ is an even number; the double indices represent summation. The second term in (3.3) gives the magnetocrystalline anisotropy energy in the form of a series in ascending powers of the magnetization components. The set of non-zero anisotropy constants $K_{n_1 n_2 n_3}$ of the order of $N = \frac{1}{2}(n_1 + n_2 + n_3)$ and the number of different exchange parameters $B_{\beta\delta}$ are governed by the crystal symmetry.

By calculating the eigenvalue spectrum of the energy of the system by means of the method described in Chap. I, Sec. 2 (see also Appendix A), we again obtain an expression of the type (2.5). In the present case

$$\mathcal{H}_0 = K_{n_1 n_2 n_3} \alpha_x^{n_1} \alpha_y^{n_2} \alpha_z^{n_3} - M_0(\alpha H), \quad (3.4)$$

and $\Delta \mathcal{H}_0$ is assumed to be zero in agreement with the conclusion reached in Appendix B; α is a unit vector of the equilibrium magnetization ($\alpha \equiv m_0$). The spin-wave energy ε_k , will be written only for those spin waves which affect the thermodynamic properties of a ferromagnet in the temperature region where

$$\kappa T \gg \frac{\mu K_N}{M_0}, \mu H. \quad (3.5)$$

For these spin waves*

$$\varepsilon_k = \frac{\mu}{M_0} \left\{ 2B_{\alpha\beta} k_\alpha k_\beta + M_0(\alpha H) - \frac{1}{2} \sum_N [2N(2N+1) - \Delta_\alpha] f_N(0) \right\}, \quad (3.6)$$

where $\Delta_\alpha = \frac{\partial^2}{\partial \alpha_x^2} + \frac{\partial^2}{\partial \alpha_y^2} + \frac{\partial^2}{\partial \alpha_z^2}$, and $f_N(0)$ represents a homogeneous polynomial of degree $2N$:

$$f_N(0) = \sum_{(n_1+n_2+n_3=2N)} K_{n_1 n_2 n_3} \alpha_x^{n_1} \alpha_y^{n_2} \alpha_z^{n_3}. \quad (3.7)$$

*The complete expression for ε_k is in the form of (2.7) and the exchange energy occurs only in α_k . When condition (3.5) is satisfied, the main contribution to the average energy of spin waves ($\varepsilon_k \sim \kappa T$) comes from the exchange interaction and, therefore, $\alpha_k \gg |\beta_k|$ and $\varepsilon_k \approx \alpha_k$. Expression (3.6) is written in this approximation.

The first term in (3.4), representing the magnetic anisotropy energy at 0°K, may be written in terms of $f_N(0)$

$$F_A(0) = \sum_N f_N(0). \quad (3.8)$$

The spin-wave energy, according to (3.6), consists of three parts: the exchange energy, the energy in an external magnetic field, and the energy related to the magnetic anisotropy forces. The condition (3.5) means, in fact, that our results are valid only in temperature regions for which the first exchange term in (3.6) is large compared with the remaining terms. It follows that we are excluding the region of very low temperatures near absolute zero ($T \lesssim 0.1-1^\circ\text{K}$).

Knowing the energy spectrum of the system (2.5) and using expressions (3.4) and (3.6), we can determine its thermodynamic potential (2.24). Taking from this potential the part depending on the direction of α with respect to the crystallographic axes, using the condition (3.5), and considering only fields H sufficiently strong to obtain saturation ($\alpha H \approx H$), we obtain the free energy of the anisotropy at temperature T :

$$F_A(T) = \sum_N \left\{ 1 - \frac{1}{2} \frac{\Delta M(T)}{M_0} [2N(2N+1) - \Delta_x] \right\} f_N(0). \quad (3.9)$$

In this formula the temperature-dependent contribution to the free energy of the anisotropy is expressed in terms of the temperature variation of the saturation magnetization:

$$\Delta M(T) = M_0 - M(T) = \frac{1}{V} \sum_k \bar{n}_k.$$

2. CUBIC AND UNIAXIAL CRYSTALS

First we shall consider cubic crystals. It is known [58] that the anisotropy energy of these crystals has one independent variable for each of the orders from 2 to 5 (i.e., for $N = 2, 3, 4$, and 5).^{*} These invariants may, in particular, be expressions of the type

$\alpha_x^{2N} + \alpha_y^{2N} + \alpha_z^{2N}$. Then, $f_N(0)$ is

$$f_N(0) = K_N(0) (\alpha_x^{2N} + \alpha_y^{2N} + \alpha_z^{2N}). \quad (3.10)$$

^{*}For $N = 1$ we have the trivial invariant $\alpha_x^2 + \alpha_y^2 + \alpha_z^2 = 1$.

It is easily seen that in this case

$$\sum_N \Delta_a f_N(0) = 2 \sum_N (N+1)(2N+1) \frac{K_{N+1}(0)}{K_N(0)} f_N(0).$$

Using the above equation, we obtain, instead of (3.9),

$$F_A(T) = \sum_N \left\{ 1 - \frac{\Delta M}{M_0} (2N+1) \left[N - (N+1) \frac{K_{N+1}(0)}{K_N(0)} \right] \right\} f_N(0). \quad (3.11)$$

Consequently,

$$F_A(T) = \sum_N f_N(T), \quad (3.12)$$

where

$$f_N(T) = K_N(T) (\alpha_x^{2N} + \alpha_y^{2N} + \alpha_z^{2N}), \quad (3.13)$$

and

$$K_N(T) = K_N(0) \left\{ 1 - \frac{\Delta M}{M_0} (2N+1) \left[N - (N+1) \frac{K_{N+1}(0)}{K_N(0)} \right] \right\} \quad (3.14)$$

is the required N th order anisotropy constant at temperature T .

Instead of (3.14) we can write the following expression for the relationship between $K_N(T)$ and $M(T)$:

$$\frac{K_N(0) - K_N(T)}{K_N(0)} = P_N \frac{M(0) - M(T)}{M(0)}, \quad (3.15)$$

where

$$P_N = (2N+1) \left[N - (N+1) \frac{K_{N+1}(0)}{K_N(0)} \right] \quad (3.16)$$

and $M(0) \equiv M_0$.

The recurrent formula (3.14) [or the equivalent formula (3.15)], valid up to $N=5$ for cubic crystals, also applies to uniaxial crystals provided the important terms in their anisotropy energy are only those of the type

$$f_N = K_N \alpha^{2N}, \quad (3.17)$$

and do not include the anisotropy in the basal plane.

For a different selection of invariants* describing the anisotropy, we obtain other relationships between $K_N(T)$ and $M(T)$, but, in general, it is not possible to deduce a recurrent formula similar to (3.14). Thus, for example, in the case of cubic crystals, the experimental data are frequently analyzed using a set of independent invariants different from that given in (3.13), e.g., the free energy of the anisotropy written in the form [59]

$$F_A = K'_2 (\alpha_x^2 \alpha_y^2 + \alpha_x^2 \alpha_z^2 + \alpha_y^2 \alpha_z^2) + K'_3 \alpha_x^2 \alpha_y^2 \alpha_z^2 + \\ + K'_4 (\alpha_x^2 \alpha_y^2 + \alpha_x^2 \alpha_z^2 + \alpha_y^2 \alpha_z^2)^2. \quad (3.18)$$

By applying formula (3.9) to expression (3.18), it is easily found that the constants K'_N also obey a relationship of the type (3.15); but now the coefficients P_N are not given by one general formula (3.16) but have the following special values:

$$P_2 = 10 - \frac{K'_3(0) + 8K'_4(0)}{K'_2(0)}, \quad P_3 = 21 - \frac{12K'_4(0)}{K'_3(0)}, \quad P_4 = 36 - \dots \quad (3.19)$$

The above result can be obtained directly from formulas (3.15) and (3.16) by assuming that the constants K_N ($N = 2, 3, 4$) in these formulas are related in the following way to the constants K'_N in expression (3.18):

$$K_2 = -\frac{1}{2} (K'_2 + K'_3), \quad K_3 = \frac{1}{3} (K'_3 - 2K'_4), \quad K_4 = \frac{1}{2} K'_4. \quad (3.20)$$

Similar calculations may be carried out for uniaxial (hexagonal) crystals for which the anisotropy energy is, instead of (3.17),

$$F_A = K'_1 (\alpha_x^2 + \alpha_y^2) + K'_2 (\alpha_x^2 + \alpha_y^2)^2 + \dots, \quad (3.21)$$

where

$$K_1 = - (K'_1 + 2K'_2), \quad K_2 = K'_2. \quad (3.22)$$

Using (3.14) and (3.22) for the constants K'_N , we again obtain an expression of the type (3.15), in which now

$$P_1 = 3 - 8 \frac{K'_2(0)}{K'_1(0)}, \quad P_2 = 10 - \dots \quad (3.23)$$

*The indeterminacy of the free energy of the magnetic anisotropy is related to the condition $\alpha_x^2 + \alpha_y^2 + \alpha_z^2 = 1$, according to which all possible invariants permitted by the crystal symmetry are not independent. Therefore, using this equation, we can exclude some of these invariants.

These results show that in the usual representation of the free energy of the anisotropy, the temperature dependence of the anisotropy constants is governed not only by their order but also by the magnitude (and sign) of the ratio of the higher- to lower-order constants at absolute zero.* Thus, for example, the first and second constants (i.e., K'_2 , K'_3 for cubic crystals and K_1 , K'_2 for hexagonal crystals) are frequently of the same order of magnitude, even at room temperature, but the second constant rises more quickly on cooling than the first [61].

Measurements of the higher anisotropy constants by available experimental methods are difficult, and the results are not very reliable [60]. Therefore, analysis of the experimental data on the temperature dependence of the anisotropy constants using theoretical relationships of the (3.15) type is at present very difficult, even for the first constants. For example, for cubic crystals, according to (3.19), the coefficient P_2 which governs the rate of variation of $K'_2(T)$ with temperature includes not only the second constant $K'_2(0)$ but also the third constant $K'_3(0)$ and, in general, constants of still higher orders. There are indications in the literature that the constant K'_1 must sometimes be allowed for in the analysis of the experimental data (for example, in the case of nickel [62]). In this respect, from the theoretical point of view, it is more convenient to write the free energy of the anisotropy of cubic crystals in the form of expressions (3.12) and (3.13) so that the formula for a lower-order constant includes, according to (3.14), only the first of the higher constants. However, the general expression (3.9), which gives the temperature dependence of the free energy of the anisotropy, allows an even simpler approach which we shall consider below.

3. EXPANSION OF THE FREE ENERGY OF THE MAGNETIC ANISOTROPY IN HARMONIC INVARIANTS

The expression (3.9) for the free energy of the magnetic anisotropy becomes considerably simpler if the homogeneous polynomials f_N , used to expand F_A , satisfy the Laplace equation

$$\Delta_x f_N = 0. \quad (3.24)$$

Such homogeneous polynomials are called harmonic.

*The possibility of the higher-order constants influencing the temperature dependence of the lower-order constants was mentioned by Zener [48] and was discussed by Carr [56] and Sato and Chandrasekhar [60].

By expanding the anisotropy energy in terms of homogeneous harmonic polynomials (which is always permissible [63]), we obtain from (3.9) and (3.24) an expression of the (3.12) type in which now

$$f_N(T) = f_N(0) \left[1 - \frac{\Delta M}{M_0} N(2N+1) \right]. \quad (3.25)$$

Consequently, the temperature dependence of any anisotropy constant that is one of the coefficients in the expansion in terms of invariant harmonic polynomials ("spherical harmonics") should obey the general law independently of crystal symmetry, and be governed only by the order $2N$ of the corresponding polynomial f_N . Thus, if

$$f_N = \sum_n \bar{K}_N^{(n)} W_{N,n}(\alpha_x, \alpha_y, \alpha_z), \quad (3.26)$$

where $W_{N,n}(\alpha_x, \alpha_y, \alpha_z)$ are independent harmonic invariants* of the order $2N$, then

$$\bar{K}_N^{(n)}(T) = \bar{K}_N^{(n)}(0) \left[1 - N(2N+1) \frac{\Delta M(T)}{M_0} \right], \quad (3.27)$$

or

$$\frac{\bar{K}_N^{(n)}(0) - \bar{K}_N^{(n)}(T)}{\bar{K}_N^{(n)}(0)} = N(2N+1) \frac{M(0) - M(T)}{M(0)}. \quad (3.28)$$

It is easily shown that relationships (3.27) and (3.28) for the temperature dependence of the "harmonic" anisotropy constants agree approximately with the Akulov-Zener formula (3.1) at low temperatures, where $\Delta M \ll M_0$. For this it is necessary to write $M(T)$ in (3.1) in the form $M(T) = M(0) - \Delta M(T)$ and leave in the right-hand part of (3.1) only a term linear in ΔM . The fact that formula (3.1) includes the absolute value of the average magnetization of the crystal, whereas our formula features the saturation magnetization, is due to the method of deducing relationship (3.27). Appendix C.I shows that, in our calculations, the assumption of saturation conditions need not be made, and if it is dispensed with this difference disappears. The same appendix also includes examples of expansions of F_A in terms of harmonic invariants for crystals of various symmetries.

The various departures of the temperature dependence $K_N(T)$ from the M^{10} law, observed in cubic crystals, may in principle

*The index n is introduced for those cases where the number of independent variants of the $2N$ th order is greater than unity.

be explained by the fact that we used the anharmonic form of (3.18) for F_A . From formula (3.19) it is evident that we may have $P_2 < 10$ or $P_2 > 10$, depending on the ratio of the magnitudes and signs of the higher-order anisotropy constants and of K'_2 . Therefore, in analyzing the experimental temperature dependence of the magnetocrystalline anisotropy of ferromagnets, it is essential to expand the free energy of the anisotropy in terms of harmonic invariants. Both the classical Akulov-Zener and the phenomenological theory of spin waves give for low temperatures the simple useful relationship (3.28), which relates the temperature variation of the anisotropy constants of various orders to the temperature variations of the magnetization. In many cases, this simple relationship is not obeyed [56, 57, 60]. However, a systematic check of this relationship and analysis of deviations from it would be of great importance because they could test the principal concepts and methods of the modern theory of ferromagnetism and thus improve the theory itself.

4. TEMPERATURE DEPENDENCE OF MAGNETOSTRICTION

We shall consider an elastic ferromagnetic medium, the state of which is represented by a local magnetization $M(\mathbf{r})$ and a deformation tensor $u_{\alpha\beta}(\mathbf{r})$. Due to magnetostriction, the magnetic and elastic states of a crystal are interdependent; in general, this interdependence applies not only to the equilibrium values of the magnetization and deformation but also to oscillations of these quantities [17, 25]. In the case of the small (harmonic) oscillations of interest to us, this relationship between magnetic and elastic properties is important only in a relatively small region of the quasimomentum space \mathbf{k} near the values of \mathbf{k} for which the acoustical vibration frequency ω_{sk} (s is the polarization index) and the frequency of magnetic oscillations ε_k/\hbar (ε_k is the spin-wave energy) are degenerate, i.e.,

$$\omega_{sk} = \varepsilon_k/\hbar.$$

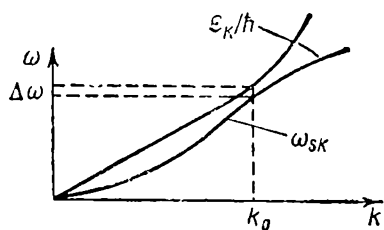


Fig. 4

The magnetoelastic interdependence “couples” the magnetic and acoustical vibrations (spin waves and phonons) and thus removes the degeneracy.

This effect is shown schematically in Fig. 4 in the simplest case where $\varepsilon_k = I\hbar k^2$ and $\omega_{sk} = c_s k$. The energy gap $\hbar\Delta\omega$ at the point k_0 , where degeneracy existed before, is governed by magnetoelastic interaction.

In considering the thermodynamic properties of a ferromagnet, we are usually interested in the temperature region where $kT \gg \hbar\Delta\omega$. This makes it possible to neglect the coupling between magnetic and elastic vibrations and, therefore, the calculation of thermodynamic properties (temperature dependences) can be carried out on the basis of an energy spectrum with two independent modes: spin waves and phonons. Our problem is to study the temperature dependence of the equilibrium deformation of a crystal.

Since elastic harmonic vibrations do not alter the equilibrium deformation, we can calculate independently the change in the magnetostrictive deformation due to magnetic vibrations.

Let us assume that the elastic vibrations represented by tensor $\sigma_{\mu\nu}$ are given. In the general case, the magnetoelastic energy density in a ferromagnet, accurate up to terms which are linear in components of the tensor $\sigma_{\mu\nu}$, can be represented in the form

$$\mathcal{H}_{\text{me}}(r) = -\lambda_{\mu\nu; n_1 n_2 n_3} \sigma_{\mu\nu} m_x^{n_1} m_y^{n_2} m_z^{n_3} - G_{\beta\gamma\mu\nu} \sigma_{\mu\nu} \frac{\partial m_\alpha}{\partial r_\beta} \frac{\partial m_\alpha}{\partial r_\gamma}. \quad (3.29)$$

The expression (3.29) can be considered the change in energy given by (3.3), caused by elastic stresses, and therefore

$$G_{\beta\gamma\mu\nu} = -\frac{\partial B_{\beta\gamma}}{\partial \sigma_{\mu\nu}}, \quad \lambda_{\mu\nu; n_1 n_2 n_3} = -\frac{\partial K_{n_1 n_2 n_3}}{\partial \sigma_{\mu\nu}}. \quad (3.30)$$

It is easily seen that the addition of the magnetoelastic contribution (3.29) to the Hamiltonian (3.3) alters the expression (3.6) for the spin-wave energy in the following way:

$$\epsilon_k = \left(\frac{\mu}{M_0} \right) \left\{ 2 (B_{\beta\gamma} - G_{\beta\gamma\mu\nu} \sigma_{\mu\nu}) k_\beta k_\gamma + M_0 H - \frac{1}{2} \sum_N [2N(2N+1) - \Delta_\alpha] [f_N(0) - \sigma_{\mu\nu} \varphi_{\mu\nu; N}(0)] \right\}, \quad (3.31)$$

where

$$\varphi_{\mu\nu; N} = \sum_{(n_1+n_2+n_3=2N)} \lambda_{\mu\nu; n_1 n_2 n_3} \alpha_x^{n_1} \alpha_y^{n_2} \alpha_z^{n_3} \quad (3.32)$$

are homogeneous polynomials of the $2N$ th order, consisting of direction cosines α_μ of the equilibrium magnetization.

Magnetic saturation is assumed here by setting $\alpha H = H$.

A term of the following type must be added to the ground-state energy (3.4):

$$- \sum_N \sigma_{\mu\nu} \varphi_{\mu\nu; N}(0). \quad (3.33)$$

If the thermodynamic potential is now written using (2.24), we can find from it the components of the magnetostrictive deformation tensor:

$$u_{\mu\nu} = - \frac{\partial \Omega}{\partial \sigma_{\mu\nu}} \bigg|_{\sigma_{\mu\nu}=0} = \sum_N \left\{ 1 - \frac{\Delta M}{2M_0} [2N(2N+1) - \Delta_x] \right\} \varphi_{\mu\nu; N}(0) + \\ + 2 \frac{M}{M_0} \sum_k G_{\beta\gamma\mu\nu} k_\beta k_\gamma (e^{-\varepsilon_k/T} - 1)^{-1}. \quad (3.34)$$

The first sum in (3.34) is the anisotropic magnetostriction responsible for the dependence of the linear dimensions and shape of a ferromagnetic sample on the direction of the magnetization; the second sum is the isotropic magnetostriction which produces an additional dependence of the sample volume on temperature (the spontaneous volume magnetostriction or thermostriction) compared with a nonferromagnetic sample, and a dependence of the volume on the magnetizing field in the intrinsic region (the intrinsic magnetostriction).

We shall consider first the anisotropic magnetostriction. If $\varphi_{\mu\nu; N}$ are harmonic polynomials for which $\Delta_x \varphi_{\mu\nu; N} = 0$, after substituting (3.32) into (3.34) the anisotropic part of the magnetostrictive deformations may be represented in the form

$$u_{\mu\nu} = \lambda_{\mu\nu; n_1 n_2 n_3}(T) x_x^{n_1} x_y^{n_2} x_z^{n_3}, \quad (3.35)$$

where the coefficients λ represent the magnetostriction constants at a temperature T ; irrespective of the crystal symmetry any magnetostriction constant of the order $N = \frac{1}{2}(n_1 + n_2 + n_3)$ satisfies the general relationship

$$\frac{\lambda_N(0) - \lambda_N(T)}{\lambda_N(0)} = N(2N+1) \frac{M(0) - M(T)}{M(0)}, \quad (3.36)$$

whose form is exactly identical with the corresponding relationship for the magnetocrystalline anisotropy constants.*

In practice, the anharmonic form of the magnetoelastic energy F_{me} is normally used. In particular, the form of F_{me} used for cubic crystals is given in Appendix C.III [formula (C.10)]. In this case, the relationship (3.36) is not, in general, satisfied and the temperature dependence of any "anharmonic" constant λ_N depends on the ratio $\lambda_{N+1}(0)/\lambda_N(0)$, etc.

*Recently, Kittel and Van Vleck [65] have shown that the Akulov-Zener law (3.1) for the anisotropy constants may be extended to the magnetostriction constants, thus independently confirming the correctness of the relationship (3.36).

For example, for the first-order constants ($N = 1$) in expression (C.10), we obtain, in place of (3.36), relationships of the form

$$\frac{\Delta\lambda_1^{(1,2)}(T)}{\lambda_1^{(1,2)}(0)} = P_1^{(1,2)} \frac{\Delta M(T)}{M(0)}, \quad (3.37)$$

where

$$P_1^{(1)} = 3 \left[1 - \frac{2\lambda_2^{(2)}(0)}{\lambda_1^{(1)}(0)} \right] \quad \text{и} \quad P_1^{(2)} = 3 \left[1 - \frac{\lambda_2^{(3)}(0)}{3\lambda_1^{(2)}(0)} \right].$$

The harmonic form, which is also given in Appendix C.III [formula (C.11)], for $N = 1$ should, according to (3.36), give a universal value of the coefficients $P_1^{(1)} = P_1^{(2)} = 3$.

Experiments show that the constants λ_2 are frequently of the same order of magnitude as the constants λ_1 . Therefore, an anharmonic analysis of the experimental data can hardly give any general relationships for the temperature dependence of the "anharmonic" constants λ_1 : it is clear from (3.37) that, depending on the relationship between $\lambda_1(0)$ and $\lambda_2(0)$, various ferromagnets may differ not only in the magnitude but also in the sign of the rate of temperature variation of the constants $\lambda_1(T)$. The advantage of the harmonic form of the magnetoelastic energy is that, by eliminating this accidental factor, it makes possible the derivation of the intrinsic relationships for the temperature dependence of magnetostriction.

It is necessary to note that, as in the case of the anisotropy constants [55], the validity of (3.36) is restricted to a narrower range of low temperatures than the range of validity of the $T^{3/2}$ law in the temperature dependence of the spontaneous magnetization. Unfortunately, there are at present no experimental data on the temperature dependence of magnetostriction at sufficiently low temperatures. Therefore, we cannot carry out a detailed comparison of relationship (3.36) with experiment. We can only mention the work of Corner and Hutchinson [144], and Birss and Lee [145], who confirmed relationship (3.36) experimentally for the first magnetostriction constant ($N = 1$) of nickel.

We shall consider very briefly some work done prior to the calculations reported above. A theoretical investigation of the temperature dependence of magnetostriction based on the spin-wave theory was carried out first by Gusev [66], who showed that at low temperatures the relationship $\Delta\lambda(T) \propto T^{1/2}$ always applies, but he did not investigate the relationship between the temperature dependences of magnetostriction and magnetization. Earlier work [67, 68], based on the molecular field approximation, led to the

following relationship between the first magnetostriction constants and the saturation magnetization

$$\frac{\lambda_1(T)}{\lambda_1(0)} = \left[\frac{M(T)}{M(0)} \right]^{P_1}, \quad (3.38)$$

where $P_1 = 2$. We note that formula (3.36) for λ_N at low temperatures (the only region where it is applicable) may also be represented in the form of expression (3.38), except that $P_1 = 3$ (the last result is implicit in Akulov's treatment [47]). Vonsovskiy's work [69] is also worth mentioning; he used a particular microscopic model to allow for the spin-orbit interaction of electrons responsible for ferromagnetism, and thus gave a basic explanation of the nonmonotonic temperature dependence of the first magnetostriction constants, sometimes observed experimentally [59, 61]. This theory has, however, several indeterminate parameters which make it difficult to test experimentally. In all the work quoted so far, the form in which the magnetoelastic energy was written was not specially considered.

We shall now deal with the isotropic (volume) magnetostriction: its temperature dependence has not yet been calculated for low temperatures.

The second sum in (3.34) can be used to find the relative change of the volume of a ferromagnet; we do this by calculating the quantity $\omega = \delta V/V_0 = \Sigma u_{\mu\mu}$ corresponding to this sum. Assuming that in the special case of a cubic crystal $B_{\beta\gamma} = B\delta_{\beta\gamma}$ and $G_{\beta\gamma\mu\nu} = G\delta_{\beta\gamma}\delta_{\mu\nu}$, we find that

$$\omega = \frac{3\Gamma(5/2)\mu G}{2\pi^2 M_0} \left(\frac{\kappa T M_0}{2\mu B} \right)^{5/2} F_{5/2}(h), \quad (3.39)$$

where $F_{5/2}(h)$ is a function given by the series in (2.32) with $\sigma = 5/2$.

When $\mu H \ll \kappa T$ ($h \ll 1$), the main contribution to ω is the spontaneous volume magnetostriction (the thermostriiction)

$$\omega_0 = \frac{3\Gamma(5/2)\xi(5/2)\mu G}{2\pi^2 M_0} \left(\frac{\kappa T M_0}{2\mu B} \right)^{5/2}. \quad (3.40)$$

The volume magnetostriction due to the intrinsic magnetization is usually represented by the quantity $\frac{\partial \omega}{\partial H}$. It is easily found from (3.39) that the latter quantity can be expressed in terms of the temperature dependence of the saturation magnetization (2.30) in the following way:

$$\frac{\partial \omega}{\partial H} = -3 \frac{\Gamma(5/2)G}{\Gamma(3/2)B} \Delta M(T, H). \quad (3.41)$$

We note that the parameter G , according to (3.30), can be defined as $G = \partial B / \partial p$, where p is the uniform pressure.

In conclusion, we shall give one more simple expression which relates physical quantities representing the principal thermodynamic properties of a ferromagnet, such as the temperature variation of the spontaneous magnetization $\Delta M_s(T)$, the spin specific heat C_s [17], the spontaneous magnetostriction w_0 , and the intrinsic magnetization $\partial w / \partial H$. If $\kappa T \gg \mu H$, we have

$$\frac{1}{3} \frac{\partial w_0}{\partial T} = -0.43 \frac{\kappa}{\mu} \frac{\partial w}{\partial H} = \frac{1}{\Theta_C} \frac{\partial \Theta_C}{\partial p} C_s = 1.91 \frac{\kappa}{\mu} \frac{1}{\Theta_C} \frac{\partial \Theta_C}{\partial p} \Delta M_s. \quad (3.42)$$

In place of the exchange coupling parameter B we have introduced here the Curie temperature Θ_C , assuming that these two quantities are directly proportional to one another.

The quantity $\frac{1}{3} \partial w_0 / \partial T = \Delta \alpha_M$ is an additional thermal expansion coefficient due to thermostriction. As expected, in accordance with the Grüneisen rule [70], this coefficient is proportional to the spin specific heat. A quantitative estimate of $\Delta \alpha_M$ can be obtained from the experimental data for the intrinsic magnetostriction [71]. For the majority of magnetic materials at room temperature, $\partial w / \partial H = 10^{-10} - 10^{-9}$ /oersted, Hence, according to (3.42), $\Delta \alpha_M = 10^{-6} - 10^{-5}$. Unfortunately, no experimental data are available on the volume magnetostriction at lower temperatures.

5. MAGNETOSTRICTIVE PARTS OF THE MAGNETIC ANISOTROPY CONSTANTS

As is known, magnetostrictive deformation alters somewhat the magnetic anisotropy constants: magnetostrictive corrections δK_N , due to anisotropic magnetostrictive deformations, are added to the purely crystallographic anisotropy constants K_N .

The additional free energy of the magnetic anisotropy can be found by determining the sum of the elastic (F_e) and magnetoelastic (F'_{me}) energies for the equilibrium values of magnetostrictive deformations. In general

$$F_e + F'_{me} = \frac{1}{2} C_{\beta\gamma\mu\nu} u_{\beta\gamma} u_{\mu\nu} + R_{\beta\gamma; n_1 n_2 n_3} u_{\beta\gamma} \alpha_x^{n_1} \alpha_y^{n_2} \alpha_z^{n_3}, \quad (3.43)$$

where $C_{\beta\gamma\mu\nu}$ are the elastic, and $R_{\beta\gamma; n_1 n_2 n_3}$ the magnetoelastic constants.

From the condition for a minimum value of (3.43) with respect to deformations $u_{\beta\gamma}$, we find

$$C_{\beta\gamma\mu\nu} u_{\mu\nu} = -R_{\beta\gamma; n_1 n_2 n_3} \alpha_x^{n_1} \alpha_y^{n_2} \alpha_z^{n_3}. \quad (3.44)$$

On the other hand, the equilibrium deformations are given by formula (3.35). Therefore,

$$R_{\beta\gamma; n_1 n_2 n_3} = -C_{\beta\gamma\mu\nu} \lambda_{\mu\nu; n_1 n_2 n_3}. \quad (3.45)$$

After substituting the equilibrium deformations into (3.43) and using (3.45), we obtain

$$\begin{aligned} \delta F_A = F_e + F_{me} = & -\frac{1}{2} C_{\beta\gamma\mu\nu} \lambda_{\beta\gamma; n_1 n_2 n_3} \lambda_{\mu\nu; n'_1 n'_2 n'_3} \times \\ & \times \alpha_x^{n_1+n'_1} \alpha_y^{n_2+n'_2} \alpha_z^{n_3+n'_3}. \end{aligned} \quad (3.46)$$

Thus, the magnetostrictive constants λ_{N_1} and λ_{N_2} , where $N_1 = \frac{1}{2}(n_1 + n_2 + n_3)$ and $N_2 = \frac{1}{2}(n'_1 + n'_2 + n'_3)$, give rise to a correction δK_N to the constant of the N th ($N = N_1 + N_2$) order

$$\delta K_N = -\frac{1}{2} C \lambda_{N_1} \lambda_{N_2}, \quad (3.47)$$

where C is the corresponding elastic constant.

In general, the temperature dependence of δK_N is the sum of the temperature dependences of C , λ_{N_1} , and λ_{N_2} . However, at low temperatures, when the elastic constants depend only slightly on temperature, we may assume that the temperature dependence of δK_N is the same as that of the product $\lambda_{N_1} \lambda_{N_2}$. This means, according to (3.36), that

$$\frac{\delta K_N(0) - \delta K_N(T)}{\delta K_N(0)} = P_N \frac{M(0) - M(T)}{M(0)}, \quad (3.48)$$

where

$$P_N = N(2N + 1) - 4N_1 N_2. \quad (3.49)$$

Here, P_N is always smaller than in the case of the crystallographic anisotropy constants K_N , since the latter are given, according to (3.28), by the following expression

$$P_N = N(2N + 1).$$

For example, $P_2 = 10$ for K_2 , the first crystallographic anisotropy constant of a cubic crystal, and $P_2 = 6$ for the correction to this constant δK_2 .

Since δK_N decreases with increase of temperature more slowly than K_N , the relative contribution of the magnetostrictive deformations to the anisotropy should be greater at higher temperatures.

Even so, the magnetostrictive correction to the magnetic anisotropy constants is, as a rule, small and is usually less than 10%. In the rare cases when this correction is comparable with the crystallographic constant, the resultant constant may have a characteristic temperature dependence due to the different temperature dependences of the two contributions (the signs of these contributions may be different as well). In particular, the sign of the anisotropy constant may be reversed or may vary nonmonotonically with temperature, i.e., it may have a maximum or a minimum [72].

CHAPTER IV

Compensated Collinear Antiferromagnetism

Antiferromagnetism represents a magnetically ordered state with the total magnetic moment equal to zero (in the absence of an external field). The discussion of this type of magnetic substance will be opened by considering the simplest case of a collinear distribution of atomic magnetic moments in a crystal lattice. The vectors of the average magnetic moments of individual lattice sites lie along the same straight line (known as the spontaneous axis of antiferromagnetism) and may differ only in their sign. This makes it possible to describe an antiferromagnet in terms of two magnetic sublattices.* Obviously, a collinear antiferromagnetic ordering of magnetic moments can occur only when certain relationships between the various exchange interaction parameters are satisfied by the magnetic atoms in the crystal. We shall assume that these relationships are indeed satisfied.

In investigating the properties of antiferromagnets, we must also take into account the magnetic anisotropy forces of relativistic origin. These forces are not only responsible for the usual anisotropy of the magnetic properties of an antiferromagnet, but they can also affect the mutual orientations and values of its magnetic moments. The result of this may be a slight noncollinearity of the magnetic moments as well as the appearance of a small uncompensated magnetic moment. If the noncollinearity does not give rise to a magnetic moment and if it is small, it has little effect on the properties of the antiferromagnet (cf. Chap. X, Sec. 2) and therefore we shall not consider it here. The appearance of an uncompensated magnetic moment in an antiferromagnet due to forces of relativistic origin need not be considered (cf. Chaps. V-IX) if the magnetocrystalline symmetry requirements are suitably formulated.

*This can be done provided the conditions referred to in Chap. I, Sec. 2 are satisfied.

1. CONDITIONS FOR COMPENSATED ANTIFERROMAGNETISM

We shall consider an antiferromagnet consisting of crystallographically equivalent atoms or ions. If the magnetic structure of this antiferromagnet is collinear or slightly noncollinear, the system of atoms or ions can be subdivided into two magnetic sublattices according to the two directions of magnetic moments.

We shall introduce total magnetic moments \mathcal{M}_1 and \mathcal{M}_2 for the two sublattices and an *antiferromagnetic vector*

$$\mathcal{L} = \mathcal{M}_1 - \mathcal{M}_2. \quad (4.1)$$

The direction of this vector defines the antiferromagnetic axis, and its relative magnitude $l = |\mathcal{L}|/\mathcal{L}_0$ may be used as a measure of long-range antiferromagnetic order. Here, \mathcal{L}_0 is the value of $|\mathcal{L}|$ at absolute zero, equal to double the magnetic moment \mathcal{M}_0 of each of the sublattices: $\mathcal{L}_0 = 2\mathcal{M}_0$.

If a collinear antiferromagnetic structure is permitted by the crystal lattice symmetry, the antiferromagnetic vector \mathcal{L} should be transformed into self-coincidence by all symmetry operations of the lattice space group. Two cases should be distinguished. If a given symmetry operation transposes atoms within the same sublattice, then \mathcal{L} is transformed like a normal axial vector. If a symmetry operation transposes atoms belonging to different magnetic sublattices [this corresponds to the transposition of the subscripts "1" and "2" in the right-hand part of (4.1)], then the vector \mathcal{L} should undergo a change of sign in addition to any properties of the axial vector. In contrast to \mathcal{L} , the total magnetic moment of the whole crystal

$$\mathcal{M} = \mathcal{M}_1 + \mathcal{M}_2, \quad (4.2)$$

if it exists at all, is invariant with respect to any transposition of atoms, and therefore is always transformed like a normal axial vector.

As already pointed out, in the present chapter we shall consider fully compensated antiferromagnetism, so that $\mathcal{M} = 0$ when $H=0$. However, in some cases the appearance of antiferromagnetic ordering in a substance, i.e., the appearance of $\mathcal{L} \neq 0$, unavoidably gives rise to $\mathcal{M} \neq 0$ by distortion of the ideal antiferromagnetic structure. This phenomenon, known as weak ferromagnetism, will be discussed in detail in Chaps. V-VII. Here, we shall point out the conditions sufficient to prevent the appearance of weak ferromagnetism.

The appearance of $\mathcal{M} \neq 0$ in antiferromagnetic crystals is related to the presence in the thermodynamic potential of terms

of the type

$$\mathcal{L}_\alpha \mathcal{M}_\beta \quad (4.3)$$

or terms of higher order in \mathcal{L} but linear in \mathcal{M} . Therefore, the absence of such mixed invariant terms is the general condition for the existence of fully compensated antiferromagnetism. Let us assume that the crystallographic and antiferromagnetic structures are such that the crystal space group of an antiferromagnet includes either inversion I or translation T , which transpose the magnetic sublattices 1 and 2 and thus, according to (4.1), reverse the sign of \mathcal{L} . Since the vector \mathcal{M} remains invariant under these operations, terms of the type (4.3) change sign and therefore are not allowed by the lattice symmetry. The zero value of \mathcal{M} can be obtained under these conditions from the following considerations of the magnetic symmetry. In these cases, there are elements IR or TR among the symmetry elements of the magnetic space group. Consequently, we should have $(IR) \mathcal{M} = \mathcal{M}$ or $(TR) \mathcal{M} = \mathcal{M}$. On the other hand, applying these symmetry operations directly to the vector \mathcal{M} , we find that $(IR) \mathcal{M} = -\mathcal{M}$ or $(TR) \mathcal{M} = -\mathcal{M}$. Hence, $\mathcal{M} = -\mathcal{M} = 0$.

It follows that antiferromagnetism is always compensated in those crystals in which all magnetic sites belong to one Bravais lattice, including those cases when the magnetic unit cell is obtained by n -fold repetition of the chemical unit cell, where $n \geq 2$.

2. UNIAXIAL ANTIFERROMAGNETS. THE HAMILTONIAN AND THE GROUND STATE

We shall consider a uniaxial (rhombohedral, tetragonal, or hexagonal) antiferromagnetic crystal. We shall assume that the principal axis of symmetry of the crystal is the Z axis. If terms of the (4.3) type, which may prevent complete compensation of the magnetic moment in the Hamiltonian, are absent, the general form of the invariant energy density of this antiferromagnet—accurate to terms not higher than the second order in the sublattice magnetization—can be written in the following form

$$\begin{aligned} \mathcal{H}(\mathbf{r}) = & \frac{A}{2} \mathbf{m}^2 + \frac{1}{2} A_{\gamma\delta} \frac{\partial m_x}{\partial r_\gamma} \frac{\partial m_x}{\partial r_\delta} + \frac{1}{2} B_{\gamma\delta} \frac{\partial l_x}{\partial r_\gamma} \frac{\partial l_x}{\partial r_\delta} + \frac{a}{2} m_z^2 + \frac{b}{2} l_z^2 - \\ & - \frac{1}{2} M_0^2 (\mathbf{m} \nabla) \int \frac{\operatorname{div} \mathbf{m}(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} - m h. \end{aligned} \quad (4.4)$$

Here

$$\mathbf{m} = \frac{\mathbf{M}_1(\mathbf{r}) + \mathbf{M}_2(\mathbf{r})}{M_0}, \quad l = \frac{\mathbf{M}_1(\mathbf{r}) - \mathbf{M}_2(\mathbf{r})}{M_0} \quad (4.5)$$

are, respectively, the local magnetization vector and the local antiferromagnetic vector divided by the maximum magnetization of the system, M_0 , i.e., by the magnetization of the system at absolute magnetic saturation. From the conditions

$$M_1^2(r) = M_2^2(r) = \left(\frac{M_0}{2}\right)^2 \quad (4.6)$$

we obtain the following two relationships for the variables m and l :

$$m^2 + l^2 = 1, \quad (ml) = 0. \quad (4.7)$$

The first three terms in (4.4) represent the exchange energy, the fourth and fifth terms give the magnetocrystalline anisotropy energy, and the penultimate and last terms give the magnetostatic energy of the volume magnetic "charge" and the energy of the antiferromagnet in an external magnetic field*

$$H = \frac{h}{M_0}.$$

Assuming that in the ground state l and m are uniform throughout the sample, we find that**

$$\frac{\mathcal{H}_0}{V} = \frac{A}{2} m^2 + \frac{a}{2} m_z^2 + \frac{b}{2} l_z^2 - mh. \quad (4.8)$$

An investigation of the energy \mathcal{H}_0 for the purpose of finding its minimum in the absence of an external field ($h = 0$), taking into account the relationships (4.7), shows that the ground state of the system is antiferromagnetic ($m = 0$ and $l = 1$) if $A > 0$. Then the spontaneous axis of antiferromagnetism (determined by the direction of the vector l) is parallel to the symmetry axis of the crystal Z if $b < 0$ and perpendicular to the Z axis if $b > 0$. We shall consider these two cases separately.

Case I: $b < 0$

In this case, the vectors l and m lie in the same plane as the external field h (let us assume that this is the YZ plane). On introducing the angle θ between the vector l and the Z axis (Fig. 5),

*The energy of the surface magnetic "charge" is not included since it is unimportant if $m \ll 1$.

**The remarks made in Chap. II, Sec I about ferromagnetism apply also to the quantum corrections to \mathcal{H}_0 due to magnetic anisotropy.

and using (4.7), \mathcal{H}_0 may be rewritten in the form

$$\frac{\mathcal{H}_0}{V} = \frac{A}{2} m^2 + \frac{a}{2} m^2 \sin^2 \theta + \frac{b}{2} (1 - m^2) \cos^2 \theta - m (h_y \cos \theta + h_z \sin \theta). \quad (4.9)$$

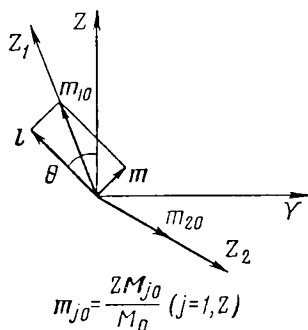


Fig. 5

We shall investigate the behavior of an antiferromagnet in an external field H only when $H \parallel Z$ or $H \perp Z$.

a) *Field H parallel to the Z axis*
($h_z = h$, $h_y = 0$)

We shall rewrite \mathcal{H}_0 in the form

$$\begin{aligned} \frac{\mathcal{H}_0}{V} &= \frac{b}{2} + \frac{A-b}{2} m^2 - \frac{b}{2} u^2 + \\ &+ \frac{a+b}{2} m^2 u^2 - h m u, \end{aligned} \quad (4.10)$$

where $u = \sin \theta$ and m are independent variables, varying within the range

$$0 \leq m, u \leq 1. \quad (4.11)$$

It is necessary to determine the points in this range which correspond to the lowest values of \mathcal{H}_0 as a function of the magnitude of h .

For convenience, we shall introduce characteristic fields defined by

$$h_{\parallel} = \sqrt{(A-b)|b|}, \quad h_{\perp} = h_{\parallel} \frac{A+b}{A-b}, \quad h'_E = A+b. \quad (4.12)$$

The results of our study thus show that the behavior of an antiferromagnet is different for different values of $a+b$; that is to say, it depends on whether $a+b > 0$ or $a+b < 0$.

1) If $a+b > 0$, then $h_{\perp} > h_{\parallel}$. In this case, the minimization of \mathcal{H}_0 gives the following relationships for the equilibrium values of $u = \sin \theta$ and m , for the magnetization in the direction of the field $M_z = M_0 m u$, and for the susceptibility $\chi = \frac{\partial M_z}{\partial H}$ as a function of the value of h at $T = 0^\circ \text{K}$.

When $0 \leq h \leq h_{\parallel}$:

$$\sin \theta = 0 \quad (l \parallel Z), \quad m = 0, \quad M_z = 0, \quad \chi_z = 0. \quad (4.13)$$

In this state, the antiferromagnetic vector l remains parallel to

the axis of symmetry of the crystal and to the field h . This state will be denoted by the indices (z) or (z/\parallel) . Here, the upper index represents the axis along which the field h is directed and the lower index the mutual orientation of the vectors l and h .

When $h_{\parallel} \leq h \leq h_{\perp}$:

$$\sin^2 \theta = \frac{h - h_{\parallel}}{h_{\perp} - h_{\parallel}}, \quad m = \left(\frac{h_{\perp}}{h_E} \right)^2 \sin^2 \theta, \quad M_z = M_0 \frac{(H - H_{\parallel}) H_{\perp}}{(H_{\perp} - H_{\parallel}) H_E}, \quad (4.14)$$

$$\chi_0 = \frac{M_0^2}{a + b}.$$

This intermediate state will be called the (z/θ) state.

When $h_{\perp} \leq h \leq h'_E$:

$$\sin \theta = 1, \quad m = \frac{h}{h_E}, \quad M_z = M_0 \frac{H}{H_E}, \quad \chi_z = \frac{M_0}{H'_E} = \frac{M_0^2}{A + a}. \quad (4.15)$$

This is the (z/\perp) state, because $l \perp h$.

When $h \geq h'_E$: $l = 0, m = 1, M_z = M_0$. This is the state of saturation along the Z axis.

The complete magnetization curve is given for this case in Fig. 6a.

The physical meaning of the fields h_{\parallel} , h_{\perp} and h'_E now becomes clear: h_{\parallel} is the field up to which the state (z/\parallel) remains stable as h is increased; h_{\perp} shows at which fields the region of stability of the (z/\perp) state begins; finally, h_E represents the field at which the absolute saturation of the antiferromagnet is reached.

It is interesting that the quantity h_E is determined mainly by the exchange forces, so that $H_E = h_E / M_0 \sim A / M_0 \equiv H_E$ is usually of the order of 10^6 - 10^7 oersteds. At the same time, the order of the values of H_{\parallel} and H_{\perp} is determined by the geometric mean of the exchange field H_E and the magnetic anisotropy field $H_A = \frac{|b|}{M_0}$: $H_{\parallel} \sim H_{\perp} \sim \sqrt{H_E H_A} \equiv H_{EA}$, which amounts to 10^4 - 10^5 oersteds.

2) If $a + b < 0$, then $h_{\perp} < h_{\parallel}$. In this case, the stability regions of the states (z/\parallel) and (z/\perp) overlap; as already pointed out, the state (z/\parallel) is stable up to $h = h_{\parallel}$, and the state (z/\perp) becomes stable at $h = h_{\perp}$. Therefore, in the field range $h_{\perp} \leq h \leq h_{\parallel}$ metastable states are possible [73]. It is easily seen that in a field

$$h_t = \sqrt{h_{\parallel} h_{\perp}} \quad (4.16)$$

the energies of the states (z/\parallel) and (z/\perp) are equal. This means that if a system passes only through thermodynamically stable states, then we have:

- a state of the (z/\parallel) type when $0 \leq h \leq h_t$,
- a state of the (z/\perp) type when $h_t \leq h \leq h_E$, and

a state of saturation along the Z axis when $h > h'_E$.

Thus, at a threshold value of the field $H_t = h_t / M_0$, the direction of the antiferromagnetic axis and the magnetization M_z change discontinuously (Fig. 6b, continuous line). If, however, the existence of metastable states is taken into account, then in a rising magnetic field the discontinuous transition to the (z/\perp) state should occur in a field $h_{\parallel} > h_t$, and in a falling magnetic field return to the previous state (z/\parallel) should occur in a field $h_{\perp} < h_t$, i.e., there should be a hysteresis (Fig. 6b).

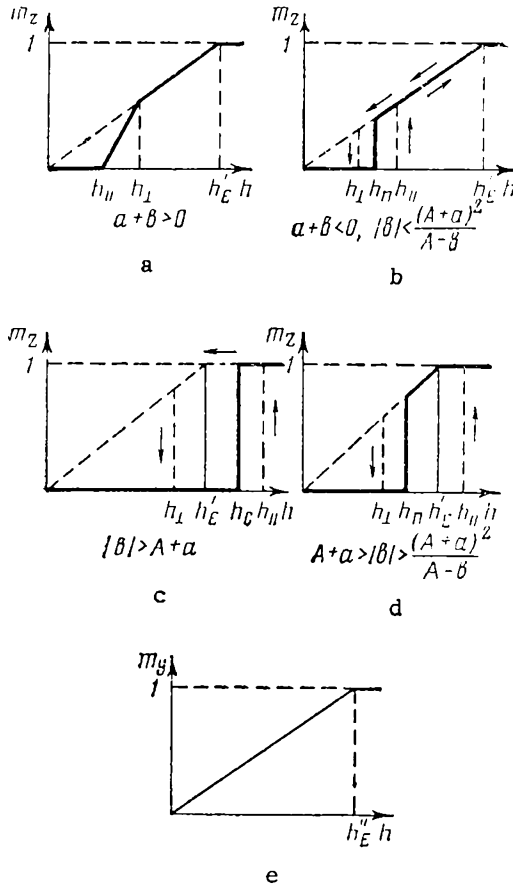


Fig. 6

The transition region $(H_{\parallel} - H_{\perp})$ is usually relatively narrow, since

$$\frac{|H_{\parallel} - H_{\perp}|}{H_t} \sim \frac{|a + b|}{A}. \quad (4.17)$$

However, in principle, we may also have a case when $h_{\parallel} > h'_E$ (and

even $h_t > h'_E$ provided always $h_\perp < h'_E$). Then $l \parallel Z$ and $m = 0$ right up to fields $h = h_\parallel$. Next, the magnetization reaches saturation ($m_z = m = 1$, cf. Fig. 6c and 6d) by a jump at $h = h_\parallel$. On reducing the field, the reverse jump to the state (z/\parallel) occurs at $h = h_\perp$. Even if the magnetization (or demagnetization) process proceeds only through equilibrium states, these jumps occur either when $h = h_t$ if $h_t < h_E$ or when $h = h_c = \frac{1}{2}(A + a - b)$ if $h_t > h'_E$ (the continuous line in Figs. 6c and 6d).

b) *Field H perpendicular to the Z axis*

In this case, the minimization of \mathcal{H}_0 given by (4.8) leads to two possible states which depend on h :

when $h \leq h''_E = A - b$, the vector l is parallel to the Z axis and

$$m_y = m = \frac{h}{A - b} \quad [\text{state } (y/\perp)]; \quad (4.18)$$

when $h \geq h''_E$, we have saturation $m_y = m = 1$ (Fig. 6e).

According to (4.18), the magnetic susceptibility in the (y/\perp) state at $T = 0^\circ\text{K}$ is

$$\chi_\perp^y = \frac{M_0^2}{A - b}. \quad (4.19)$$

It is worth noting the anisotropy of the "transverse" susceptibility ($h \perp l$) for the states (z/\perp) and (y/\perp):

$$\frac{1}{\chi_\perp^z} - \frac{1}{\chi_\perp^y} = \frac{a + b}{M_0^2}. \quad (4.20)$$

Measurement of the difference between the reciprocals of the susceptibilities for these two cases makes it possible to determine directly the anisotropy constant $a + b$. This determines also the type of magnetization curve (Fig. 6a or Fig. 6b) along the Z axis, because this curve depends on the sign of $a + b$.

Case II: $b > 0$.

In this case, the antiferromagnetic vector l lies always in the basal plane at right angles to the external field H . The magnetic moment m is directed along H and its magnitude is found from the condition of minimum energy \mathcal{H}_0 in (4.8), which in this case is

$$\frac{\mathcal{H}_0}{V} = \frac{A}{2} m^2 + \frac{a}{2} m^2 \cos^2 \psi - mh, \quad (4.21)$$

where ψ is the angle between h and the Z axis.

From the equation $\partial \mathcal{H}_0 / \partial m = 0$, we find

$$m = \frac{h}{A + a \cos^2 \psi}. \quad (4.22)$$

The magnetic susceptibility depends on the direction of H :

$$\chi_{\perp}^{\psi} = \frac{M_0^2}{A + a \cos^2 \psi}. \quad (4.23)$$

The difference between the reciprocals of the susceptibilities along the crystal axis and at right angles to it gives the anisotropy constant a :

$$\frac{1}{\chi_{\perp}^z} - \frac{1}{\chi_{\perp}^y} = \frac{a}{M_0^2}. \quad (4.24)$$

Our discussion of the ground state of an antiferromagnet and its dependence on the magnetizing field did not include quantum corrections related to the zero-point oscillation energy $\Delta \mathcal{H}_0$. A calculation of $\Delta \mathcal{H}_0$ for two cases—the longitudinal and transverse magnetization [the states $(z \parallel \parallel)$ and $(y \perp \perp)$ —is given in Appendix D.II.

In the former case ($l \parallel H$), $\Delta \mathcal{H}_0$ is independent of H and therefore does not alter the classical result for the longitudinal susceptibility, i.e., $\chi_{\parallel} = 0$ at $T = 0^\circ \text{K}$. In the latter case ($l \perp H$) $\Delta \mathcal{H}_0$ depends strongly on H , and therefore, to find the equilibrium angle between the sublattice magnetizations which determines the ground state of an antiferromagnet in a transverse field, one must, in general, minimize the sum of the energies $\mathcal{H}_0 + \Delta \mathcal{H}_0$. Moreover, the sublattice magnetizations themselves are somewhat lower due to the zero-point oscillations than the classical values obtained a priori ($M_{10} = M_{20} = M_0/2$). All this leads to the result that the transverse magnetic susceptibility at $T = 0^\circ \text{K}$ is smaller than the classical values given by (4.15), (4.19), etc.

Actual calculation of these quantum corrections must allow for the periodic nature of the quantities A_k and B_k related to exchange interactions and considered as functions of the quasi-momentum k (see Sec. 3 below). In principle, this allowance may be made by extending the method of calculating the spin-wave spectrum of a ferromagnet, given in Appendix B, to the case of an antiferromagnet. However, the problem of the ground state of an antiferromagnet has been dealt with in numerous papers in which the model of discrete spin sublattices has been used [74–76]. The most correct approach to the problem is that of P'u Fu-ch'u [76], who invoked the Green's function method developed by Bogolyubov and Tyablikov [77]. From the cited work, it follows that the

quantum correction to the transverse magnetic susceptibility of an antiferromagnet at $T = 0^\circ\text{K}$ reaches, under the most unfavorable conditions (when the spin of one atom is $S = \frac{1}{2}$), 10–20%, decreasing as $1/S$ with increasing S . The nature of the qualitative classical relationships remains unaffected by the quantum corrections. From the phenomenological point of view, such corrections are not very important because the phenomenological theory considers principally not the absolute values of physical properties (which are given in terms of the phenomenological constants of the theory) but the relationships between the various properties and the qualitative laws governing these relationships (for example, temperature and field dependences).

3. UNIAXIAL ANTIFERROMAGNETS. SPIN-WAVE SPECTRUM AND RESONANCE PROPERTIES

We shall now consider the spin-wave spectrum of a uniaxial antiferromagnet. To calculate the spin-wave spectrum, we shall use expressions of the (1.15) and (1.18) type to introduce the operators $b_r^{(j)}$ and $b_r^{+(j)}$ ($j = 1, 2$) into the Hamiltonian (4.4). Then we shall isolate the term \mathcal{H}_2 which is quadratic with respect to these operators and reduce it to the diagonal form:

$$\mathcal{H}_2 = \Delta\mathcal{H}_0 + \sum_k (\varepsilon_{1k} n_{1k} + \varepsilon_{2k} n_{2k}). \quad (4.25)$$

In this way, we obtain two spin-wave modes of energies ε_{1k} and ε_{2k} . The results of such a calculation are given below for each of the state considered in Sec. 2. Appendix D.I includes the derivation of the expressions for ε_{1k} and ε_{2k} in the general case, i.e., for any value of the angle θ (between the equilibrium vector l and the Z axis) and the equilibrium value of m , which together determine the ground state of an antiferromagnet when the equilibrium vectors l and m lie in the same plane as the Z axis. With one exception [the formula (4.39) and its variants], the formulas given below for ε_{1k} and ε_{2k} are the special cases of the general expression given by (D.5) in Appendix D. Appendix D.II presents a calculation of the correction $\Delta\mathcal{H}_0$ to the ground-state energy of an antiferromagnet due to zero-point oscillations.

We shall consider first the state (z/\parallel) . In this state, $\theta = m = 0$; therefore, according to (D.5), we have

$$\begin{aligned} \varepsilon_k^{(1,2)} = \frac{\mu}{M_0} \{ & (B_k + |b|)(A + A_k + |b| + 2q) + h^2 \pm \\ & \pm 2\sqrt{(B_k + |b|)(A + A_k + |b| + q)h^2 + (B_k + |b|)^2 q^2} \}^{1/2}. \end{aligned} \quad (4.26)$$

The following notation is used here:

$$A_k = A_{\gamma\delta} k_\gamma k_\delta = A_\perp (k_x^2 + k_y^2) + A_z k_z^2,$$

$$B_k = B_{\gamma\delta} k_\gamma k_\delta = B_\perp (k_x^2 + k_y^2) + B_z k_z^2,$$

and the quantity $q = \pi M_0^2 (k_x^2 + k_y^2) / k^2$ represents the magnetostatic energy [the penultimate term in (4.4)].

It is evident from (4.26) that the magnetostatic energy is responsible for the fact that the splitting of the spin-wave spectrum into two modes does not disappear even when $h = 0$. The relative size of the magnetostatic energy correction is small. This is particularly clear if we assume that $h = 0$; then

$$\begin{aligned} \varepsilon_{1k} &= \frac{\mu}{M_0} [(B_k + |b|)(A + A_k + |b| + 4q)]^{1/2}, \\ \varepsilon_{2k} &= \frac{\mu}{M_0} [(B_k + |b|)(A + A_k + |b|)]^{1/2}. \end{aligned} \quad (4.27)$$

Thus, the magnetostatic energy ($\sim 4\pi M_0^2$) is a term additional to the exchange interaction ($\sim A$) and therefore has practically no influence on the energy of the spin wave. However, the magnetostatic splitting of the spin-wave spectrum may be important in some dynamic processes in antiferromagnets.*

If we neglect the magnetostatic energy (i.e., if we assume that $q = 0$) then, instead of the general expression (4.26), we have

$$\varepsilon_k^{(1,2)} = \frac{\mu}{M_0} [(B_k + |b|)(A + A_k + |b|)]^{1/2} \pm \mu H. \quad (4.28)$$

In particular, assuming that $k = 0$, we obtain the energy gaps, i.e., the minimum energies necessary to excite spin waves corresponding to uniform oscillations of the magnetization of an antiferromagnet; these energies determine two frequencies of uniform antiferromagnetic resonance:

$$\omega_{1,2} = \frac{\varepsilon_0^{(1,2)}}{\hbar} = \gamma (H_\parallel \pm H). \quad (4.28')$$

The state considered, i.e., (z/\parallel) , is stable in fields up to $H \leq H_\parallel$.

*Moreover, as shown by Popov [78] and clearly evident from formula (4.26), the magnetostatic energy may affect the nature of the dependence of the spin-wave energy on the magnitude of the external field H when $h^2 \leq \frac{B_k + |b|}{A} q^2$. This, however, does not affect the thermodynamic properties of an antiferromagnet, nor the frequencies of uniform antiferromagnetic resonance.

Let us now assume that our system is in the state (z/\perp) ; then according to (4.15), $\theta = \frac{\pi}{2}$ and $m = \frac{h}{A+a}$. In this case, the spin-wave energies of (D.5) become:*

$$\begin{aligned} \varepsilon_{1k} &= \frac{\mu}{M_0} \left\{ (A + A_k) \left[B_k + b + \left(\frac{h}{h_E} \right)^2 (A + A_k - B_k - b) \right] \right\}^{1/2}, \\ \varepsilon_{2k} &= \frac{\mu}{M_0} \left\{ B_k \left[A + A_k + a - \left(\frac{h}{h_E} \right)^2 (A + A_k - B_k + a) \right] \right\}^{1/2}. \end{aligned} \quad (4.29)$$

We note that these expressions are valid in the case $b < 0$ if $h_{\perp} \leq h \leq h_E$, and in the case $b > 0$ if $0 \leq h \leq h_E$. In the state (z/\perp) , one of the modes has no energy gap, i.e., when $k = 0$ we have

$$\omega_1 = \frac{\varepsilon_{10}}{\hbar} = \gamma H_{EA} \sqrt{\frac{H^2}{H_{\perp}^2} + 1}, \quad \omega_2 = \frac{\varepsilon_{20}}{\hbar} = 0, \quad (4.30)$$

where $H_{EA}^2 = A|b|/M_0$; under the square root the plus sign should be taken for $b > 0$ and the minus sign for $b < 0$.

The absence of an energy gap in one of the spin-wave modes in the (z/\perp) state arises from the fact that in the original Hamiltonian (4.4) we did not allow for terms of higher order in l responsible for the anisotropy in the basal plane. If such terms (fourth-order terms for tetragonal crystals and sixth-order terms for hexagonal crystals) are allowed for, a small gap appears even for ε_{2k} . This gap may be considerably smaller than the gap for ε_{1k} but it may be larger than the corresponding gap in a uniaxial ferromagnet. This is true because in an antiferromagnet the gap is determined not by the anisotropy field of fourth or sixth order, $H_A^{(4,6)}$, but by the geometric mean of $H_A^{(4,6)}$ and the exchange field H_E

$$\varepsilon_{20} = \mu \sqrt{H_E H_A^{(4,6)}} \quad (4.31)$$

for tetragonal $[H_A^{(4)}]$ and hexagonal $[H_A^{(6)}]$ crystals (see also Chaps. VI and VII).

To allow for the anisotropy in the basal plane of tetragonal crystals, it is necessary to add to the Hamiltonian (4.4) the following term

$$\frac{1}{2} \int l_x^2 l_y^2, \quad (4.32)$$

*If we again neglect the magnetostatic energy. In general, we shall neglect this energy in all considerations. Detailed accounts of the influence of the magnetostatic energy on the properties of an antiferromagnet are given elsewhere [78, 79].

where f is the fourth-order anisotropy constant.* It is easily shown that this leads to a change in the spin-wave energy ε_{2k} of (4.29), which represents a simple replacement of the multiplier B_k in front of the square bracket by another multiplier $(B_k + f)$. This means that the energy gap for ε_{2k} is in the form of (4.31) with

$$H_A^{(4)} = \frac{\mu}{M_0} f. \quad (4.33)$$

We shall now consider saturation along the Z axis: $m_z = m = 1$, $h = h_z$. According to (D.5), we have in this case

$$\begin{aligned} \varepsilon_{1k} &= \frac{\mu}{M_0} \left[\left(A_k - a + h + 4\pi M_0^2 \frac{k_x^2 + k_y^2}{k^2} \right) (A_k - a + h) \right]^{1/2}, \\ \varepsilon_{2k} &= \frac{\mu}{M_0} (h - h'_E + B_k). \end{aligned} \quad (4.34)$$

It is easily seen that, except for the sign, ε_{1k} is identical with the corresponding formula (2.11) for a uniaxial ferromagnet.** When $k = 0$, we have

$$\omega_1 = \frac{\varepsilon_{10}}{h} = \gamma (H - H_a), \quad \omega_2 = \frac{\varepsilon_{20}}{h} = \gamma (H - H'_E), \quad (4.35)$$

where $H_a = a / M_0$.

Next, bearing in mind that for the (y / \perp) state, $\theta = 0$, $m = \frac{h}{A - b}$, $h = h_y$, the spin-wave energy (D.5) of this state may be written in the form:

$$\varepsilon_{1k} = \frac{\mu}{M_0} \left\{ (A + A_k + |b|) \left[B_k + |b| + \left(\frac{h}{h''_E} \right)^2 (A + A_k - B_k + a) \right] \right\}^{1/2}, \quad (4.36)$$

$$\varepsilon_{2k} = \frac{\mu}{M_0} \left\{ (B_k + |b|) \left[A + A_k + |b| - \left(\frac{h}{h''_E} \right)^2 (A + A_k - B_k + |b|) \right] \right\}^{1/2},$$

or, for $k = 0$

$$\begin{aligned} \omega_1 &= \frac{\varepsilon_{10}}{h} = \gamma \sqrt{H_{\parallel}^2 + H^2 \frac{H_{\perp}}{H_{\parallel}}}, \\ \omega_2 &= \frac{\varepsilon_{20}}{h} = \gamma H_{\parallel} \sqrt{1 - \left(\frac{H}{H''_E} \right)^2}. \end{aligned} \quad (4.37)$$

*Here and later, we shall define the order of the anisotropy constant as the power of the invariant of l or m with which the constant is associated; this is a departure from the notation adopted in Chap. III. We shall assume that $f > 0$, and, consequently, in the ground state $l \parallel X$ or $l \parallel Y$.

**Here, we do not allow for the demagnetizing field of the sample surface.

We shall quote now the results of a calculation of the spin-wave energy for the case $b > 0$, when H lies in the basal plane. In this case, the vector $l \perp H$ (assuming $H \parallel X$) also lies in the basal plane ($\theta = \psi = \frac{\pi}{2}$), and, according to (4.22),

$$m = \frac{h}{A}, \text{ when } h \leq A \text{ [state } (x \perp)] \quad (4.38)$$

and

$$m = 1 \text{ when } h \geq A.$$

The spin-wave energies for $h \leq A$ are given by the expressions .

$$\begin{aligned} \varepsilon_{1k} &= \frac{\mu}{M_0} \left\{ (A + A_k + a) \left[B_k + \left(\frac{h}{A} \right)^2 (A + A_k - B_k) \right] \right\}^{1/2}, \\ \varepsilon_{2k} &= \frac{\mu}{M_0} \left\{ (B_k + b) \left[A + A_k - \left(\frac{h}{A} \right)^2 (A + A_k - B_k) \right] \right\}^{1/2}, \end{aligned} \quad (4.39)$$

so that when $k = 0$

$$\begin{aligned} \omega_1 &= \frac{\varepsilon_{10}}{h} = \gamma H \sqrt{1 + \frac{a}{A}} = \gamma H \sqrt{\frac{\chi_{\perp}^x}{\chi_{\perp}^z}}, \\ \omega_2 &= \frac{\varepsilon_{20}}{h} = \gamma H_E A \sqrt{1 - \left(\frac{H}{H_E} \right)^2}, \end{aligned} \quad (4.40)$$

where $H_E = A / M_0$.

If we allow for the anisotropy in the basal plane, then the expression for ω_1 has an additional term, which depends on the azimuthal angle φ_H of the direction of H . For example, for a tetragonal crystal, instead of (4.40), we have

$$\omega_1 = \gamma \left[H^2 \left(1 + \frac{a}{A} \right) + H_E H_A^{(4)} \cos 4\varphi_H \right]^{1/2}. \quad (4.41)$$

Here, we assume that $H > \sqrt{H_E H_A^{(4)}}$, which is necessary to ensure that the vector m is always directed along H .

For saturation in the basal plane (when $h > A$)*

$$\begin{aligned} \varepsilon_{1k} &= \frac{\mu}{M_0} \{ (A_k + a + h) (A_k + h) \}^{1/2}, \\ \varepsilon_{2k} &= \frac{\mu}{M_0} \{ (B_k + h - A + b) (B_k + h - A) \}^{1/2}. \end{aligned} \quad (4.42)$$

*If $b < 0$, then these expressions apply to $h > (A - b)$. The magnetostatic energy is not included in (4.42).

The corresponding frequencies for $k = 0$ are, consequently, given by

$$\begin{aligned}\omega_1 &= \gamma \sqrt{H(H + Ha)}, \\ \omega_2 &= \gamma \sqrt{(H - H_E'')(H - H_E)}.\end{aligned}\quad (4.43)$$

It is convenient to rewrite the above expressions for the spin-wave energies of the various states in a simpler approximate form making the following assumptions:*

a) we shall assume that $H_{\parallel} = H_{\perp} = H_t = \sqrt{A|b|}/M_0 \equiv H_{EA}$, bearing in mind the relatively narrow range of fields ($H_{\parallel} - H_{\perp}$) of (4.17);

b) we shall consider fields which are not too strong, so that $H \ll H_E$;

c) we shall neglect the quantity A_k compared with A and the anisotropy (in the k -space) of the quantity B_k , assuming that $B_k = Bk^2$ and $\left(\frac{\mu}{M_0}\right)^2 AB = I^2$.

The results may be presented in the following form.

I. $b < 0$. *Spontaneous antiferromagnetic axis parallel to the Z axis*

a) The (z/\parallel) state, i.e., $H \parallel Z$ and $H < H_{EA}$:

$$\varepsilon_k^{(1,2)} = \sqrt{(\mu H_{EA})^2 + I^2 k^2} \pm \mu H. \quad (4.44)$$

b) The (z/\perp) state, i.e., $H \parallel Z$ and $H > H_{EA}$:

$$\varepsilon_{1k} = \sqrt{\mu^2 (H^2 - H_{EA}^2) + I^2 k^2}, \quad \varepsilon_{2k} = Ik \sqrt{1 - \frac{H_{EA}^2}{H^2}}. \quad (4.45)$$

c) The (y/\perp) state, i.e., $H \perp Z$:

$$\begin{aligned}\varepsilon_{1k} &= \sqrt{\mu^2 (H_{EA}^2 + H^2) + I^2 k^2}, \\ \varepsilon_{2k} &= \sqrt{[(\mu H_{EA})^2 + I^2 k^2] \left(1 - \frac{H^2}{H_E^2}\right)}.\end{aligned}\quad (4.46)$$

*We must point out that it is best to make these simplifications in the later stages of calculating the thermodynamic quantities (particularly the magnetization and magnetic susceptibility) using general expressions for these quantities. Otherwise, important terms may be lost.

II. $b > 0$. *Spontaneous antiferromagnetic axis perpendicular to the Z axis*

a) The (z/\perp) state, i.e., $H \parallel Z$:

$$\varepsilon_{1k} = \sqrt{\mu^2 (H_{EA}^2 + H^2) + I^2 k^2}, \quad \varepsilon_{2k} = Ik \sqrt{1 - \frac{H^2}{H_E^2}}. \quad (4.47)$$

b) The (x/\perp) state, i.e., $H \parallel X$:

$$\varepsilon_{1k} = \sqrt{(\mu H)^2 + I^2 k^2},$$

$$\varepsilon_{2k} = \sqrt{[(\mu H_{EA})^2 + I^2 k^2] \left(1 - \frac{H^2}{H_E^2}\right)}. \quad (4.48)$$

A comparison of all the above spin-wave energy formulas shows that the energy gaps (and, consequently, the antiferromagnetic resonance frequencies) and even the form of their dependence on the external field, may differ considerably for different states and different field directions.* It is worth pointing out here that the measurement of antiferromagnetic resonance frequencies and the investigation of their dependence on the field are the most direct methods of determining the physical constants of a ferromagnet. These methods used for single crystals give all the principal parameters describing the magnetic properties of an antiferromagnet.

In this connection, it was interesting to establish the conditions (the selection rules) which must be satisfied for the excitation of various frequencies. We are mainly interested in the direction of the high-frequency field h_ω (for a given constant magnetizing field H) needed to excite uniform oscillations of the frequencies ω_1 or ω_2 .

The operator for the energy of interaction of an antiferromagnet with a uniform high-frequency magnetic field h_ω is given by the expression

$$\mathcal{H}_\omega = -M_0 h_\omega \int m(r) dr. \quad (4.49)$$

By introducing second quantization by means of relationships of the (1.15) type, and also using expressions (1.18) and (4.5), we can

*The expressions for the energy spectrum and resonance frequencies of the intermediate state (z/θ) , realizable over a narrow range of fields $H_{||} \leq H \leq H_{\perp}$ when $(a+b) > 0$, are not given here because they are cumbersome. The appropriate expressions for $\varepsilon_k^{(1,2)}$ may be obtained from (D.5) by substituting θ and m given by (4.14).

find the quantum transitions of frequencies ω_1 and ω_2 for which the transition probabilities are not equal to zero.

We shall consider first the (z/\parallel) state. For this state

$$m_x = \frac{M_{1x_1} + M_{2x_2}}{M_0}, \quad m_y = \frac{M_{1y_1} - M_{2y_2}}{M_0}, \quad m_z = \frac{M_{1z_1} - M_{2z_2}}{M_0}. \quad (4.50)$$

Expressing $M_{j\alpha_j}$ in terms of the second quantization operators $b_r^{(j)}$ and $b_r^{\dagger(j)}$ by means of relationships of the (1.15) type and using the Fourier components of these operators, we have, in place of (4.49),

$$\mathcal{H}_\omega = - \left(\frac{\mu M_0 V}{4} \right)^{1/2} [(b_1 + b_1^\dagger + b_2 + b_2^\dagger) h_\omega^{(x)} + \\ + i (b_1 - b_1^\dagger - b_2 + b_2^\dagger) h_\omega^{(y)}]. \quad (4.51)$$

Here, $b_j \equiv b_{k=0}^{(j)}$, and we leave in \mathcal{H}_ω only those terms that are linear in the operators b_j because our intention is to consider the processes of excitation of a single spin wave (of frequency ω_1 or ω_2). Using the results in Appendix D.II, we shall now change from b_j and b_j^\dagger to the operators $\xi_j = \xi_{k=0}^{(j)}$ and $\xi_j^\dagger = \xi_{k=0}^{\dagger(j)}$ for which the quadratic form of \mathcal{H}_2 is diagonal:

$$b_1 = U_0 \xi_1 - V_0 \xi_2^\dagger, \quad b_1^\dagger = U_0^\dagger \xi_1^\dagger - V_0^\dagger \xi_2, \\ b_2 = U_0 \xi_2 - V_0 \xi_1^\dagger, \quad b_2^\dagger = U_0^\dagger \xi_2^\dagger - V_0^\dagger \xi_1, \quad (4.52)$$

where the transformation coefficients U_0 and V_0 are given by the relationships (D.12) with $k = 0$. Operators ξ_j^\dagger and ξ_j are the creation and annihilation operators for spin waves of frequencies $\omega_j = \varepsilon_{k=0}^{(j)}/\hbar$. After substituting (4.52) into (4.51), we obtain

$$\mathcal{H}_\omega = - \frac{1}{2} \left\{ \mu M_0 V \sqrt{\frac{|b|}{A + |b|}} \right\}^{1/2} [(h_\omega^{(x)} + i h_\omega^{(y)}) \xi_1 + \\ + (h_\omega^{(x)} - i h_\omega^{(y)}) \xi_2 + (h_\omega^{(x)} - i h_\omega^{(y)}) \xi_1^\dagger + (h_\omega^{(x)} + i h_\omega^{(y)}) \xi_2^\dagger]. \quad (4.53)$$

It is evident from (4.53) that in the (z/\parallel) state the oscillations of frequencies ω_1 and ω_2 of (4.29) may be excited only in the presence of components of the field h_ω perpendicular to the Z axis (and therefore to the vector l and the field H). To excite oscillations of the frequency $\omega = \omega_1$, it is necessary to use a right-handed (clockwise-polarized) wave; to excite oscillations of frequency $\omega = \omega_2$, we must use a left-handed (counterclockwise-polarized)

wave. It follows that, in principle, we can magnetize an antiferromagnet longitudinally by a transverse circularly polarized magnetic field. In fact, a circularly polarized wave transverse to the antiferromagnetic axis may excite oscillations of one type only (even when $H = 0$ and $\omega_1 = \omega_2$) which violates the equilibrium between the average numbers of spin waves $n_1 = \langle \xi_1^\dagger \xi_1 \rangle$ and $n_2 = \langle \xi_2^\dagger \xi_2 \rangle$. It follows from expressions (4.50) and (4.52) that a longitudinal magnetic moment should appear

$$\mathcal{M}_z = -\mu (n_1 - n_2).$$

It is necessary to estimate the magnitude of this effect. This can easily be done by calculating the transverse high-frequency components of the magnetizations M_1 and M_2 . Then

$$M_z = \frac{\mathcal{M}_z}{V} = M_{1z} + M_{2z} \simeq - \frac{(M_{1x}^2 + M_{1y}^2) - (M_{2x}^2 + M_{2y}^2)}{M_0}.$$

Such a calculation, based on the solution of the equations of motion of the (1.8) type for M_j in a circularly polarized high-frequency field

$$h_\omega^{(x)} = h_0 \cos \omega t, \quad h_\omega^{(y)} = h_0 \sin \omega t,$$

is given in the Appendix D.III. This transverse high-frequency field produces a longitudinal magnetization (in the absence of a longitudinal field, $H = 0$) the relative magnitude of which at resonance is given by the simple formula

$$\frac{M_z}{M_0} = - \left(\frac{|b|}{A + |b|} \right)^{1/2} \left(\frac{\gamma h_0}{\Delta \omega} \right)^2 \equiv - \left(\frac{H_A}{H_E} \right)^{1/2} \left(\frac{h_0}{\Delta H} \right)^2, \quad (4.54)$$

where $\Delta \omega$ is the resonance line width, and $\Delta H = \Delta \omega / \gamma$. Thus, to observe this effect, we need an antiferromagnet with a sufficiently narrow resonance line and a strong electromagnetic field. For example, to obtain magnetizations of the order of 0.1% of the saturation value (which represents about 1 gauss for $M_0 \approx 10^3$ gauss) the ratio $h_0 / \Delta H$ must be $\approx 10\%$ for $H_A / H_E \approx 10^{-2}$. Despite the complete absence of work devoted exclusively to searching for antiferromagnets with narrow resonance lines, there have already been reports of resonance curves with $\Delta H \approx 10$ oersteds [80] and therefore, we may expect that the effect discussed here should be capable of experimental observation.

Similarly, we can find the conditions for antiferromagnetic resonance in the case when a steady field is perpendicular to the antiferromagnetic axis. We shall consider the (y/\perp) state. Then the energy \mathcal{H}_ω of (4.49) may be represented in terms of creation and annihilation operators (ξ_j^\dagger and ξ_j) for spin waves with frequencies

ω_j [(4.36)] in the following form (Appendix D.II):

$$\mathcal{H}_\omega = -(\mu M_0 V)^{1/2} \{h_\omega^{(x)} (U_1 - V_1) (\xi_1 + \xi_1^\dagger) + \\ + i h_\omega^{(y)} l (U_2 - V_2) (\xi_2 + \xi_2^\dagger) - i h_\omega^{(z)} m (U_1 + V_1) (\xi_1 - \xi_1^\dagger)\}. \quad (4.55)$$

Here, the transformation coefficients U_j and V_j are given by the relationships (D.22) and (D.23) for $k = 0$. The following selection rules for antiferromagnetic resonance in the (y/\perp) state follow from (4.45):

1) at the frequency $\omega = \omega_1$ (4.36₁), the first resonance mode is excited in the presence of an h_ω component perpendicular to the steady magnetizing field H and therefore perpendicular to m :

2) at the frequency $\omega = \omega_2$ (4.36₂), the second mode is excited if the high-frequency field has a component parallel to the steady field H .

We can show that the resonance conditions are of exactly the same form for all the other states when $l \perp H$; when $h_\omega \perp H$, only the first mode of frequency ω_1 can be excited, and when $h_\omega \parallel H$, only the second mode of frequency ω_2 .

Table 1 presents the resonance conditions and formulas, together with schematic plots of the dependence of the resonance frequencies on the magnetizing field, for all states considered here. In the saturation region ($m = 1$), there is only one resonance frequency (ω_1) since oscillations at the other frequency (ω_2) cannot be excited by a uniform electromagnetic field.

In general, the available experimental data on antiferromagnetic resonance verify the theory presented here. Unfortunately, these data are scarce because for many antiferromagnets the resonance conditions require either very strong constant fields ($H \approx H_{EA}$) or very high alternating field frequencies lying in the millimeter or infrared region. For example, the resonance of MnF_2 [81] and Cr_2O_3 [82] was investigated in the millimeter range using fields of about $(1-5) \times 10^4$ oersteds,* and the resonance of FeF_2 [83] and NiO [84] in the infrared region using wavelengths of $(2-3) \times 10^{-2}$ cm, which correspond to fields of the order of $(3-5) \times 10^5$ oersteds (assuming $\hbar\omega = \mu H$).

Antiferromagnetic resonance at centimeter wavelengths may be observed in those antiferromagnets whose antiferromagnetic axis is in the basal plane. Since, however, several of such antiferromagnets exhibit weak ferromagnetism, we shall consider them later (Chap. IX).

*The field H_{EA} for MnF_2 and Cr_2O_3 was 94 and 60 kilooersteds, respectively.

Table 1

$b < 0$		$b > 0$	
$H \parallel Z$	$\omega_1(\hbar\omega \perp H)$ $(\hbar\omega \parallel H)$	$H \parallel Z$	$\omega_1(\hbar\omega \perp H)$
ω_2	$\omega_2(\hbar\omega \parallel H)$	$\omega_2(\hbar\omega \parallel H)$	
$I \parallel Z$ $\frac{\omega_1}{\gamma} = H_{EA} + H$ $\frac{\omega_2}{\gamma} = H_{EA} - H$	$H_{EA} \quad I \perp Z \quad H_E$ $\frac{\omega_1}{\gamma} = \sqrt{H^2 - H_{EA}^2}$ $\frac{\omega_2}{\gamma} = 0$ $m = m_Z = 1$ $\frac{\omega_1}{\gamma} = H - H_a$	$I \perp Z$ $\frac{\omega_1}{\gamma} = \sqrt{H_{EA}^2 + H^2}$ $\frac{\omega_2}{\gamma} = 0$ H_E $m = m_Z = 1$ $\frac{\omega_1}{\gamma} = H - H_a$	
$H \perp Z$	$\omega_1(\hbar\omega \perp H)$ $\omega_2(\hbar\omega \parallel H)$	$H \perp Z$	$\omega_1(\hbar\omega \perp H)$ $\omega_2(\hbar\omega \parallel H)$
$I \parallel Z$ $\frac{\omega_1}{\gamma} = \sqrt{H^2 + H_{EA}^2}$ $\frac{\omega_2}{\gamma} = H_{EA} \sqrt{1 - H^2/H_E^2}$	$m = m_{\perp} = 1$ $\frac{\omega_1}{\gamma} = \sqrt{H(H + H_a)}$	$I \perp Z$ $\frac{\omega_1}{\gamma} = H \sqrt{1 + a/A}$ $\frac{\omega_2}{\gamma} = H_{EA} \sqrt{1 - H^2/H_E^2}$ $m = m_{\perp} = 1$ $\frac{\omega_1}{\gamma} = \sqrt{H(H + H_a)}$	

Note. The table lists the resonance frequencies and conditions for a uniaxial antiferromagnet. For simplicity, it is assumed that

$$H_{EA} = H_t = H_{\parallel} = H_{\perp} = \sqrt{A|b|}/M_0,$$

$$H_E = H'_E = H''_E = A/M_0.$$

The frequency $\omega_2 \neq 0$, if the anisotropy in the basal plane is taken into account.

4. UNIAXIAL ANTIFERROMAGNETS. THERMODYNAMIC PROPERTIES

The thermodynamic properties of antiferromagnets of interest to us (e.g., the temperature dependence of the spin specific heat and of the magnetic susceptibility) may be calculated using the thermodynamic potential of spin waves [cf., for example, the last term in (2.24)]:

$$\Omega_s = \kappa T \sum_{j, k} \ln (1 - e^{-\varepsilon_{jk}/\kappa T}), \quad (4.56)$$

where ε_{jk} are the corresponding spin-wave energies for the given antiferromagnetic state. The spin contribution to the specific heat C_s (in a constant field H) and the temperature-induced change of the magnetic susceptibility $\Delta\chi = \chi(T) - \chi(0)$ are expressed in terms of Ω_s in the following way:

$$C_s = -T \frac{\partial^2 \Omega_s}{\partial T^2} = \frac{\partial}{\partial T} \sum_{j, k} \varepsilon_{jk} \bar{n}_{jk}, \quad (4.57)$$

$$\Delta\chi = -\frac{\partial^2 \Omega_s}{\partial H^2} = -\sum_{j, k} \left[\frac{\partial^2 \varepsilon_{jk}}{\partial H^2} \bar{n}_{jk} - \left(\frac{\partial \varepsilon_{jk}}{\partial H} \right)^2 \frac{\partial \bar{n}_{jk}}{\partial \varepsilon_{jk}} \right], \quad (4.58)$$

where $\bar{n}_{jk} = [\exp(\varepsilon_{jk}/\kappa T) - 1]^{-1}$ is the average number of spin waves of the j th type in the k state.

We shall calculate C_s and $\Delta\chi$ on the basis of approximate expressions for the spin-wave energy (4.44)–(4.47). In some cases, the more general formulas will also be discussed.

We note that for each mode of the spin-wave spectrum, the whole temperature range ($0 < T \ll \Theta_N$) may be divided arbitrarily into three parts:

- 1) $\kappa T \ll \varepsilon_{j0}$, the region where the thermal motion energy is small compared with the energy gap;
- 2) $\kappa T \sim \varepsilon_{j0}$, the transition region where this energy and the gap are comparable;
- 3) $\kappa T \gg \varepsilon_{j0}$, the region where the energy gap is small compared with κT .

In the first region, the appropriate mode of spin waves makes a small contribution to $\Delta\chi$ and C_s which decreases exponentially on cooling (there is also a multiplier which depends less strongly on temperature). In these cases, we shall assume that $C_s \approx 0$ and $\Delta\chi \approx 0$, bearing in mind that, in fact, this exponential temperature dependence occurs. In the other limiting case, when $\kappa T \gg \varepsilon_{j0}$, $C_s(T)$ and $\Delta\chi(T)$ may be represented as a series in powers of T , but we shall use only the first term of this series. Finally, in the intermediate temperature region $C_s(T)$ and $\Delta\chi(T)$ cannot be expressed in terms of simple functions of T (although the integrals

obtained for this case and depending on T as a parameter can be tabulated). We shall not write down the general expressions since consideration of the two limiting cases should give us qualitative features of the temperature dependence of C_s and $\Delta\chi$ for various states.*

We shall give the results of our calculations of C_s and $\Delta\chi$ for various states, both when $b < 0$ and $b > 0$.

I. *Spontaneous antiferromagnetic axis is the crystal axis, $b < 0$.*

A. The (z/\parallel) state: $H \parallel Z, H < H_{EA}$.

a) $\mu H_{EA} \ll \kappa T$:

$$C_s = aT^3, \quad a = \left(\frac{4\pi^2}{15}\right) \kappa \left(\frac{\kappa}{T}\right)^3, \quad (4.59)$$

$$\Delta\chi = \alpha T^2, \quad \alpha = \frac{(\mu\kappa)^2}{3I^3}. \quad (4.60)$$

b) $\mu H_{EA} \gg \kappa T, \mu(H_{EA} - H) \ll \kappa T$:

$$C_s = a_1 T^{3/2}, \quad a_1 = \frac{15(2\mu H_{EA}\kappa)^{3/2}\kappa}{32\pi^{3/2}I^3}, \quad (4.61)$$

$$\Delta\chi = 2\sqrt{2}\pi^2 \frac{\mu^2}{I} \frac{\kappa T}{I} \frac{\mu H_{EA}}{I} \left(\frac{H_{EA}}{H_{EA} - H}\right)^{1/2} \quad (4.62)$$

c) $\mu(H_{EA} - H) \gg \kappa T$:

$$C_s \approx 0, \quad \Delta\chi \approx 0. \quad (4.63)$$

B. The (z/\perp) state: $H \parallel Z, H > H_{EA}$.

a) $\mu\sqrt{H^2 - H_{EA}^2} \ll \kappa T$:

$$C_s = aT^3, \quad (4.64)$$

$$\Delta\chi = -\frac{1}{4}\alpha T^2. \quad (4.65)$$

b) $\mu\sqrt{H^2 - H_{EA}^2} \gg \kappa T$:

$$C_s = \frac{1}{2}aT^3, \quad (4.66)$$

$$\Delta\chi = \frac{\pi^2}{10}\alpha T^2 \left(\frac{\kappa T}{\mu H_E}\right)^2. \quad (4.67)$$

*However, we must point out that it is not a rare case when the temperature region in which $\epsilon_{j0} \ll \kappa T \ll 0_N$ does not exist at all. A more complete presentation of the formulas for $C_s(T)$ and $\Delta\chi(T)$ with a larger number of terms is given in a recent paper of Bar'yakhtar and Popov [79].

C. The (y/\perp) state, $H \perp Z$.

a) $\mu \sqrt{H_{EA}^2 + H^2} \ll \kappa T$:

$$C_s = aT^3, \quad (4.68)$$

$$\Delta\chi = -\frac{1}{4} \alpha T^2. \quad (4.69)$$

b) $\mu H_{EA} \ll \kappa T \ll \mu \sqrt{H_{EA}^2 + H^2}$:

$$C_s = \frac{1}{2} aT^3, \quad (4.70)$$

$$\Delta\chi = \frac{\pi^2}{10} \alpha T^2 \left(\frac{\kappa T}{\mu H_E} \right)^2. \quad (4.71)$$

c) $\kappa T \ll \mu H_{EA}$:

$$C_s \approx 0, \quad \Delta\chi \approx 0. \quad (4.72)$$

II. *Spontaneous antiferromagnetic axis lies perpendicular to the crystal axis, $b > 0$.*

A. The (z/\perp) state, $H \parallel Z$.

a) $\mu \sqrt{H_{EA}^2 + H^2} \ll \kappa T$:

$$C_s = aT^3, \quad (4.73)$$

$$\Delta\chi = -\frac{1}{4} \alpha T^2. \quad (4.74)$$

b) $\mu \sqrt{H_{EA}^2 + H^2} \gg \kappa T$:

$$C_s = \frac{1}{2} aT^3, \quad (4.75)$$

$$\Delta\chi = \frac{\pi^2}{10} \alpha T^2 \left(\frac{\kappa T}{\mu H_E} \right)^2. \quad (4.76)$$

B. The (x/\perp) state, $H \perp Z$.

a) $\kappa T \gg \mu H, \mu H_{EA}$:

$$C_s = aT^3, \quad (4.77)$$

$$\Delta\chi = -\frac{1}{4} \alpha T^2. \quad (4.78)$$

b) $\mu H \ll \kappa T \ll \mu H_{EA}$:

$$C_s = \frac{1}{2} aT^3, \quad (4.79)$$

$$\Delta\chi = -\frac{1}{4} \alpha T^2. \quad (4.80)$$

$$c) \mu H \gg \kappa T \gg \mu H_{EA}:$$

$$C_s = \frac{1}{2} \alpha T^3, \quad \Delta\chi = \frac{\pi^2}{10} \alpha T^2 \left(\frac{\kappa T}{\mu H_E} \right)^2. \quad (4.81)$$

We shall now formulate some conclusions which follow from these results and which are of interest from the viewpoint of experimental verification.

1. The spin specific heat C_s of an antiferromagnet is directly proportional to T^3 if at least one of the spin-wave modes has an energy gap $\varepsilon_{j0} \ll \kappa T$. The coefficient of proportionality should increase (with increase in temperature) doubling with the transition from the temperature region in which this inequality is satisfied only for one spin-wave mode to the temperature region in which the inequality applies to both spin-wave modes (for the (z/\perp) state with $b < 0$, we make the transition from formula (4.66) to formula (4.64); for the (z/\perp) and (x/\perp) states with $b > 0$, we make the transitions from (4.75) to (4.73) and from (4.79) or (4.81) to (4.77), respectively).

This relationship was observed experimentally by Kalinkina and Borovik-Romanov in MnCO_3 , who were the first to show the existence of two spin-wave spectrum modes in an antiferromagnet using specific heat measurements [85].

2. It is worth noting the change in the value of C_s and in the nature of its temperature dependence when the magnetizing field H is altered. This is particularly important in the case when the field is directed along the spontaneous antiferromagnetic axis Z ($b < 0$) in the temperature region $\kappa T \ll \mu H_{EA}$: in weak fields [formula (4.63)] the specific heat is vanishingly small, but it increases with increase in H , and when $\mu (H_{EA} - H) \ll \kappa T$ the specific heat becomes directly proportional to $T^{3/2}$ [formula (4.61)]; at the threshold field $H = H_{EA}$ (change of the type of state), C_s falls sharply and becomes proportional to T^3 [formula (4.64)].* Thus, on passing through the threshold field there is a considerable magnetocaloric effect due to the discontinuous change of the specific heat of the antiferromagnet.

3. The spin specific heat and the nature of its temperature dependence for a uniaxial single crystal may be altered greatly not only by varying the field intensity but also by changing the direction of the crystal axis with respect to a fixed direction of the field H . For example, the specific heat drops sharply to a

*The ratio of the specific heats above (C_s^\perp) and below (C_s^\parallel) the threshold field H_{EA} is $C_s^\perp/C_s^\parallel \sim 10 \left(\frac{\kappa T}{\mu H_{EA}} \right)^{3/2}$. When $\kappa T \ll \mu H_{EA}$, this ratio may be much smaller than unity.

vanishingly small value on transition from the (z/\parallel) state (the "b" case) or from the (z/\perp) state (the cases "a" and "b") to the (y/\perp) state (the "c" case). This means that if the spin specific heat is a considerable fraction of the total specific heat of an antiferromagnet, the sample temperature should change considerably with adiabatic rotation of the crystal 90° from the $Z \parallel H$ position to the $Z \perp H$ position (or conversely).

4. A comparison of formula (4.60) with (4.65), and of (4.60) with (4.69) yields the following simple relationship between the temperature-induced changes in the longitudinal ($H \parallel l$) and transverse ($H \perp l$) magnetic susceptibilities:

$$\Delta\chi_{\perp} \simeq -\frac{1}{4} \Delta\chi_{\parallel}. \quad (4.82)$$

Although special investigations for the purpose of verifying the above relationship have not yet been carried out, the available experimental data [74, 86, 87, 133] indicate clearly that it is not satisfied. The quantity $\Delta\chi_{\parallel} \equiv \chi_{\parallel}(T)$ in some cases [86, 87, 133] satisfies the " T^2 law," while $\Delta\chi_{\perp}$ varies much less with temperature than predicted by formula (4.82) or may be constant.

As already pointed out (cf. the first footnote in Sec. 4 of Chap. IV), the temperature region satisfying the condition $\mu H_{EA} \ll \kappa T \ll \kappa \Theta_N$ necessary to obtain the simple power laws $C_s \sim T^3$ and $\Delta\chi \sim T^2$ may not exist at all for the states with $l \parallel Z$ in which both spin-wave modes have energy gaps $\varepsilon_{j0} \sim \mu H_{EA}$. Therefore, uniaxial antiferromagnets for which $l \perp Z$ in the ground state, are of special interest in the verification of the theory of spin waves because, in such antiferromagnets, the energy gap is practically nonexistent for one of the spin-wave modes (this gap is governed by the external field or the energy of the magnetic anisotropy of higher orders).

However, we note that even for antiferromagnets with $l \perp Z$, the theoretically predicted quadratic decrease of the transverse susceptibility with increase of temperature was not confirmed experimentally.

5. According to the formula (4.62), the magnetic susceptibility of the (z/\parallel) state for $\kappa T \ll \mu H_{EA}$ depends on the magnitude of the field near its threshold value H_{EA} and has a singularity in the limit $H \rightarrow H_{EA}$. This is fully expected, since at $H \geq H_{EA}$ the (\parallel/z) state becomes unstable. It would be interesting to check experimentally the theoretically predicted dependence for this case: $\Delta\chi_{\parallel} \equiv \chi \sim (H_{EA} - H)^{-1/2}$.

6. The temperature dependence of the transverse susceptibility is anisotropic for antiferromagnets whose spontaneous antiferromagnetic axis lies in the basal plane ($b > 0$). In the temperature

region $\kappa T \ll \mu H_{EA}$, the susceptibilities χ_{\perp} along two mutually perpendicular directions (along the principal axis of the crystal Z and at right angles to it, for example along the X axis) should have completely different forms and opposite signs. According to formulas (4.76) and (4.80), $\Delta\chi_{\perp}^z \sim T^4$ and is positive, while $\Delta\chi_{\perp}^x \sim T^2$ and is negative; moreover, $\Delta\chi_{\perp}^z \ll |\Delta\chi_{\perp}^x|$. Similar results should apply to antiferromagnets with $b < 0$ in fields stronger than the threshold, $H \gg H_{EA}$ [compare formulas (4.65) and (4.72)].

7. Finally, the relationship between the magnetic susceptibility and the spin specific heat of an antiferromagnet is of fundamental importance in the experimental verification of the spin-wave theory. For example, for the $(z' \parallel)$ state when $\kappa T \gg \mu H_{EA}$, we have, according to formulas (4.59) and (4.60),

$$\frac{C_s}{T\chi_{\parallel}} = \frac{4\pi^2}{5} \left(\frac{\kappa}{\mu} \right)^2 \approx 3.8 \times 10^8. \quad (4.83)$$

The above relationship, if valid, can be used to calculate from the magnetic susceptibility the contribution of spin waves to the total specific heat of an antiferromagnet.

We shall now consider the possible reasons why the “ T^2 law” is not satisfied by the temperature dependence of the transverse susceptibility χ_{\perp} , and why there are deviations from the expression (4.82) which relates $\Delta\chi_{\parallel}$ to $\Delta\chi_{\perp}$.

We shall first deal with inaccuracies in our calculations that may have affected the relationship (4.83), although apparently to a slight extent.

In the state with $l \perp H$, the ground state represented by the angle between the equilibrium sublattice magnetizations may be affected by temperature. Therefore, it would have been more accurate to calculate the equilibrium value of this angle (or the related equilibrium value of m) not by minimizing \mathcal{H}_0 (or even $\mathcal{H}_0 + \Delta\mathcal{H}_0$), as done above, but by minimizing the total thermodynamic potential of the system Ω , consisting of the ground-state energy and the thermodynamic potential of spin waves Ω_s , with an indeterminate value of the parameter m .^{*} This calculation is carried out in Appendix D.IV. It was found that the effect considered here does indeed reduce somewhat the absolute value of $\Delta\chi_{\perp}$, but the correction is directly proportional to T^4 and is thus a correction of a higher order that need not be included in our approximation. This correction is important only if the expansion of $\Delta\chi_{\perp}$ in terms of temperature begins with a term proportional to T^4 [formulas (4.67),

^{*}Compare this with the corresponding calculation of the magnetization curve of a uniaxial ferromagnet along a hard direction (Sec. 3, Chap. II).

(4.71), (4.76) and (4.81)]. Then we must add the following term to the right-hand parts of the listed formulas:

$$\left(\frac{H_E}{64 M_0} \right) \alpha^2 T^4.$$

If, in the calculation of $\Delta\chi_{\perp}$ —for example, for the (y/\perp) state—we use, instead of the approximate expressions (4.46), the more general expressions (4.36) for the spin-wave energy, we find that a multiplier $\frac{A(A+a)}{(A-b)^2}$ appears in the formula (4.69) for $\Delta\chi_{\perp}$. This multiplier alters the relationship (4.82) between $\Delta\chi_{\parallel}$ and $\Delta\chi_{\perp}$. However, it may differ considerably from unity only in very rare cases, when at least one of the anisotropy constants (a or b) is comparable with the exchange parameter A .*

Finally, the relationship between $\Delta\chi_{\parallel}$ and $\Delta\chi_{\perp}$ may be influenced also by the zero-point oscillation energy and higher-order terms in the expansion of the Hamiltonian in terms of the operators b_r and b_r . Oguchi [75] and P'u Fu-ch'u [76] have shown that these refinements may alter the ratio $\Delta\chi_{\perp}/\Delta\chi_{\parallel}$ by about 10-20%, tending to increase it. The nature of the temperature dependence remains unaffected.

Thus, the reason for the departure from the relationship (4.82) remains unclear. It is possible that the fault lies not in the calculations but in the initial assumptions of the theory. The most doubtful assumption is that the modulus of the local magnetization vector (4.6) of each of the sublattices is constant.

5. ANTIFERROMAGNETISM IN ORTHORHOMBIC AND CUBIC CRYSTALS

The principal magnetic properties of uniaxial antiferromagnets—the presence of a threshold field for the magnetization along the antiferromagnetic axis, the two modes of spin waves with energy gaps ε_{j0} determined by the geometric mean values of the exchange and anisotropy energies, and the nature of the temperature dependence of the magnetic susceptibility and of the spin specific heat at temperatures $\kappa T \gg \varepsilon_{j0}$ —are also typical of antiferromagnetic crystals of other crystal symmetries. To confirm this, we shall consider briefly antiferromagnets of orthorhombic and cubic symmetries.

In the orthorhombic case, the energy density of the formula (4.4) should be modified as follows: the terms with constants

*This may happen for some layered structures.

a and b , representing the magnetocrystalline anisotropy, should be replaced by terms of the type*

$$\mathcal{H}_A(\mathbf{r}) = \frac{a_1}{2} m_x^2 + \frac{a_3}{2} m_z^2 + \frac{b_1}{2} l_x^2 + \frac{b_3}{2} l_z^2. \quad (4.84)$$

Depending on the relationship between the magnitudes and signs of the anisotropy constants b_1 and b_3 , the spontaneous antiferromagnetic axis is directed along one of the orthorhombic axes of the crystal (which can be taken to lie along the coordinate axes X, Y, Z). For example, when

$$b_3 < 0 \quad \text{and} \quad b_1 - b_3 > 0 \quad (4.85)$$

the spontaneous antiferromagnetic axis is directed along the Z axis. This ground state with magnetization $m = 0$ is retained also on the application of an external magnetic field $H \parallel Z$, so long as this field does not exceed the threshold value**

$$H_{EA} \simeq -\frac{\sqrt{A(b_1 - b_3)}}{M_0}. \quad (4.86)$$

When $H = H_{EA}$, the antiferromagnetic vector \mathbf{l} rotates discontinuously, becoming perpendicular to H , so that $\mathbf{l} \parallel X$ if $b_1 < 0$, and $\mathbf{l} \parallel Y$ if $b_1 > 0$. Then we find that magnetization occurs along the H direction:

$$m_z = m = \frac{h}{A + a_3 - b_1} \quad \text{or} \quad \frac{h}{A + a_3}. \quad (4.87)$$

If the magnetizing field is $H \perp Z$, then \mathbf{l} remains parallel to Z right up to saturation; then, if $H \parallel X$,

$$m = m_x = \frac{h}{A + a_1 - b_3}, \quad (4.88)$$

and, if $H \parallel Y$,

$$m = m_y = \frac{h}{A - b_3}. \quad (4.89)$$

The characteristic feature of the spin-wave spectrum of orthorhombic antiferromagnets, as compared with uniaxial crystals,

*Moreover, the exchange energy tensors $A_{\gamma\delta}$ and $B_{\gamma\delta}$ contain three different components.

**As in the case of uniaxial crystals, we can have metastable states but we shall not consider them here.

is the fact that the two spin-wave modes have different energies even when $H = 0$ (and without allowing for the magnetostatic interaction). When $H = 0$, according to Appendix D.IV [formula (D.36)], we have

$$\begin{aligned}\varepsilon_{1k} &= \frac{\mu}{M_0} [(A + A_k - b_3) (B_k + b_1 - b_3)]^{1/2}, \\ \varepsilon_{2k} &= \frac{\mu}{M_0} [(A + A_k + a_1 - b_3) (B_k - b_3)]^{1/2}.\end{aligned}\quad (4.90)$$

In contrast to the magnetostatic splitting [Sec. 3, formula (4.27)], the splitting due to the magnetic anisotropy is not small. In particular, when $k = 0$, this splitting, equal to the difference between the energy gaps of the spin waves

$$\varepsilon_{10} - \varepsilon_{20} = \frac{\mu}{M_0} [V A (b_1 - b_3) - V A |b_3|], \quad (4.91)$$

is, in general, of the same order of magnitude as the energy gaps themselves. The energy gaps in an orthorhombic crystal are always governed by the geometric mean values of the exchange energy and the second-order magnetic anisotropy energy.

Appendix D.V contains a calculation of the energy of the spin waves of an orthorhombic crystal in the field $H \neq 0$ directed along the antiferromagnetic axis ($l \parallel Z$). Here, we shall give the approximate expressions for the spin-wave energies only for the case of transverse magnetization* when $H \perp l$. If, for example, $H \parallel X$, then (for $h \ll A$)

$$\begin{aligned}\varepsilon_{1k} &= \frac{\mu}{M_0} [(b_1 - b_3) A + h^2 + l^2 k^2]^{1/2}, \\ \varepsilon_{2k} &= \frac{\mu}{M_0} \left[\left(1 - \frac{h^2}{A^2} \right) (|b_3| A + l^2 k^2) \right]^{1/2}.\end{aligned}\quad (4.92)$$

As in the case of uniaxial crystals, the first mode of the spin waves makes a considerable contribution to the transverse magnetic susceptibility ($\Delta\chi_{\perp} \sim T^2$ when $\varepsilon_{10} \ll \kappa T$). At antiferromagnetic resonance, this mode is excited in crossed fields ($h_{\omega} \perp H$). Because of the weak field dependence, the second spin-wave mode can contribute to $\Delta\chi_{\perp}(T)$ only a small term proportional to T^4 (when $\kappa T \gg \varepsilon_{20}$). At resonance, this mode should be excited in parallel fields ($h_{\omega} \parallel H$). In general, using thermodynamic properties, it can easily be shown that all the relationships for the temperature

*These expressions will be needed for comparison with the case of weak ferromagnetism in orthorhombic crystals (cf. Chap. VIII).

dependence of C_s and $\Delta\chi$ obtained in Sec. 4 for uniaxial crystals, when $\kappa T \gg \varepsilon_{j0}$ ($j = 1, 2$), apply to orthorhombic antiferromagnets as well. In the other limiting cases, $\kappa T \ll \varepsilon_{j0}$, the specific heat and the temperature-dependent term in the susceptibility should decrease exponentially.

Orthorhombic crystals have a lower symmetry than uniaxial crystals, but cubic crystals have a higher symmetry. For the latter, the anisotropy energy (including terms of an order no higher than the fourth) has the form*

$$\mathcal{H}_A(r) = \frac{1}{2}b(l_x^2l_y^2 + l_x^2l_z^2 + l_y^2l_z^2) + \frac{1}{2}a(l_x^2m_x^2 + l_y^2m_y^2 + l_z^2m_z^2). \quad (4.93)$$

In the present case, the spontaneous antiferromagnetic axes are either [001] axes, i.e., X, Y , or Z axes if $b > 0$, or [111] axes, i.e., the body diagonals of a cube if $b < 0$. Let us assume that $b > 0$ and that initially the antiferromagnetic vector l (in $H = 0$) is directed along the Z axis. We shall consider again the longitudinal and transverse magnetization cases.

In the ground state with $H \parallel l$

$$m = 0,$$

and with $H \perp l$

$$m = \frac{h}{A}. \quad (4.94)$$

If we now allow for weak harmonic oscillations about these states, then for $H \parallel l$ the anisotropy energy of the formula (4.93) can be represented approximately in the form

$$\mathcal{H}_A \simeq \frac{1}{2}b - \frac{1}{2}bm^2 - \frac{1}{2}bl_z^2. \quad (4.95)$$

Comparing (4.95) with the corresponding terms in the expression (4.4) for the uniaxial crystal energy, we see that the spin-wave energies of a cubic crystal can be obtained from the corresponding expression (4.28) for a uniaxial crystal if b is replaced with $-b$ and A is replaced with $(A - b)$. Moreover, it is necessary to allow for the fact that for a cubic crystal

$$A_k = A_1k^2 \quad \text{and} \quad B_k = Bk^2.$$

*Taking into account the conditions of formula (4.7), we retain only the independent invariants and, moreover, restrict ourselves to fields which are not too strong ($m \ll 1$) thereby omitting the invariant of $m_x^2m_y^2 + m_x^2m_z^2 + m_y^2m_z^2$.

Consequently, we have

$$\varepsilon_k^{(1,2)} = \frac{\mu}{M_0} [(b + Bk^2)(A + A_1k^2)]^{1/2} \pm \mu H. \quad (4.96)$$

When $k = 0$

$$\varepsilon_0^{(1,2)} = \hbar\omega_{1,2} = \frac{\mu}{M_0} \sqrt{Ab} \pm \mu H. \quad (4.97)$$

Since one of the energies in (4.97) becomes negative if $H > H_{EA}^{(4)} = \sqrt{Ab}/M_0$, it follows that the state with $l \parallel H$ is stable only if $H < H_{EA}^{(4)}$.

Let us assume now that $l \perp H$. This happens when either the applied field is initially perpendicular to l or if we reach this state from the $l \parallel H$ state when $H > H_{EA}^{(4)}$. Again, we shall consider small oscillations about the ground state represented by (4.94). We find that the anisotropy energy can, in this case, be represented by (for $h \ll A$)

$$\mathcal{H}_A \simeq \frac{1}{2} b (1 - m^2 - l_2^2) + am_2^2.$$

This means that the spin-wave spectrum of this state may be obtained from the corresponding spectrum of a uniaxial antiferromagnet given by formula (4.36) for the (y/\perp) state by replacing in (4.36) b with $-b$, a with $2a$, and A with $(A - b)$, where $h_E = A$. The approximate expressions obtained on the assumption that $h, a, b \ll A$ are of exactly the same form as (4.46).

The thermodynamic relationships and resonance frequencies of a cubic crystal in states $l \parallel H$ and $l \perp H$ remain practically the same as for a uniaxial crystal in the states (z/\parallel) and (y/\perp) , respectively. The only difference is that, for a cubic crystal, the threshold field is $H_{EA}^{(4)}$ and consequently the energy gaps for spin waves are governed by the geometric mean values of the exchange energy and the fourth-order anisotropy energy (not the second-order energy). Consequently, H_{EA} may be one or two orders of magnitude smaller than for uniaxial and orthorhombic crystals. This means that antiferromagnetic resonance in cubic crystals may sometimes be observed in the centimeter range of electromagnetic waves.

CHAPTER V

General Conditions for the Existence of Weak Ferromagnetism in Antiferromagnetic Crystals

As already pointed out, anisotropic magnetic forces may disturb the strict collinearity of the magnetic moments in an antiferromagnet. The noncollinearity may be accompanied by a finite spontaneous magnetic moment. If such a moment does exist, we speak of weak (noncollinear) ferromagnetism in the antiferromagnet; if there is no such moment, we are simply dealing with slightly noncollinear antiferromagnetism.

Let us consider first the case of weak ferromagnetism. For simplicity, we shall ignore the departure from collinearity of the magnetic moments that were parallel in the original antiferromagnetic structure. Then the whole noncollinearity is due to the departure from the strict antiparallelism of the magnetizations of the two sublattices, each of which consists of magnetic moments directed in an identical way. The effects due to the departure from collinearity of formerly parallel magnetic moments and, in particular, the slightly noncollinear antiferromagnetism, will be discussed in Chap. X. To describe these effects, we need more than two magnetic sublattices.

A weak uncompensated spontaneous magnetic moment may exist also in an antiferromagnet with collinear magnetic structure because of some "nonequivalence" of the magnetic sublattices which describe this structure. This will also be discussed when considering the properties of weak ferromagnets.

1. STATEMENT OF THE PROBLEM. CONDITIONS IMPOSED BY TRANSLATIONS AND AN INVERSION CENTER

In 1956, Borovik-Romanov and Orlova [88] explained the nature of the weak ferromagnetism detected in manganese and cobalt

carbonates (MnCO_3 and CoCO_3), by a model of an antiferromagnet, in which the directions of the magnetic sublattice magnetizations are not strictly antiparallel but make a small angle with one another.* Dzyaloshinskiy [14] justified the possibility of such a magnetic state from the point of view of the symmetry of magnetic crystals. He showed that the weak ferromagnetism of rhombohedral crystals with MnCO_3 and $\alpha\text{-Fe}_2\text{O}_3$ (hematite) structures, and of tetragonal crystals with the rutile structure (for example, NiF_2), is an intrinsic property of these crystals related to their magnetocrystalline structure.** The smallness of the spontaneous moment is due to the fact that it appears as the result of the perturbing action of the magnetic anisotropy forces (i.e., forces of relativistic origin) on the magnetic structure of an antiferromagnet established by exchange forces (i.e., by forces of electrostatic nonrelativistic origin).

Later experimental and theoretical studies [92-106, 133] (including several theoretical papers written by the present author himself and in conjunction with others [32-40]) have shown that weak ferromagnetism is a very common phenomenon. For a given crystallographic structure of an antiferromagnet in a certain state, weak ferromagnetism occurs as frequently as the cubic magnetic anisotropy in cubic crystals and the tetragonal magnetic anisotropy in tetragonal crystals.

Since weak ferromagnetism is due to the magnetic anisotropy forces, the magnetic properties of weak ferromagnets are strongly anisotropic. As a rule, a weak ferromagnetic crystal exhibits spontaneous magnetization only along certain crystallographic directions, retaining the properties of a normal antiferromagnet along other directions. For this reason, the phenomenon of weak ferromagnetism may appear in very different ways in crystals of different symmetries (it may even differ for crystals of the same symmetry but of different type of antiferromagnetic ordering) so that a discussion of the properties of weak ferromagnets without reference to their actual magnetocrystalline structure [104, 105] would be pointless.

Theoretical papers on the problem of weak ferromagnetism may be divided into two groups. One group [14, 34-39, 92-98] considers actual magnetic crystals for which the crystallographic space groups are known and magnetic atom positions established. Then, assuming that the magnetic and chemical unit cells of a

*Somewhat earlier, a similar idea was put forward by Matarrese and Stout [89], who explained the weak ferromagnetism of NiF_2 .

**The most complete neutron diffraction studies of the magnetic structure of transition-metal carbonates and fluorides, in connection with the problem of weak ferromagnetism, were made by Alikhanov [90, 91].

crystal are identical, the possibility of the existence of weak ferromagnetism is investigated by determining the antiferromagnetic structures permitted by the given magnetic atom positions, and in which this possibility could be realized. Then, the expressions for the free energy (or the Hamiltonian) written down from the symmetry considerations, are used to deal with the actual physical properties of a weakly ferromagnetic crystal. In this approach, the whole procedure is repeated not only for each space group but also for each of the crystallographic positions of the magnetic atoms within the same space group.

The second group of papers [2, 99] deals with the general theory of the magnetic symmetry of crystals: they list all the magnetic symmetry classes which permit the existence of a spontaneous magnetic moment (irrespective of the origin of this moment) and then the symmetry of the tensors describing macroscopic properties are established, etc. Using this approach, in particular that given in [99], it is possible to establish whether weak antiferromagnetism may exist if the actual antiferromagnetic structure represented by a given magnetic space group is known. However, the problem is not tied up with the original crystallographic structure and with the crystallographic positions of the magnetic atoms. Moreover, the symmetry considerations by themselves cannot give any quantitative relationships for the properties of weak ferromagnets.

Modifying somewhat the approach used in the first group of papers, we can attempt to obtain certain general conditions for the existence of weak ferromagnetism in antiferromagnets. These conditions are imposed by the presence of a given symmetry element in the crystallographic space group of a magnetic material, by the positions of the magnetic atoms in the lattice with respect to this symmetry element, and, finally, by the nature of magnetic ordering with respect to the same element (i.e., by the possibility of transforming into self-coincidence, by means of this symmetry element, the sites with parallel or antiparallel magnetic moments). In this way, we can construct a table which gives a very simple classification of weak ferromagnets in accordance with the type of invariants in their magnetic energy responsible for the appearance of spontaneous magnetization.

We shall again assume that an antiferromagnet consists of a system of magnetic atoms in crystallographically equivalent lattice sites. We shall further assume that the exchange forces acting between these atoms establish by themselves a collinear antiferromagnetic structure. Such a system can be described by two magnetic moment densities, $M_1(\mathbf{r})$ and $M_2(\mathbf{r})$, which correspond to the two magnetic sublattices in the discrete model.

The most important of the conditions for the existence of weak ferromagnetism was in fact obtained in Sec. 1 of Chap. IV. We have formulated there a definite requirement which the magnetic structure of an antiferromagnet must satisfy to ensure that weak ferromagnetism is absent. The opposite condition is in fact one of the necessary conditions for the existence of weak ferromagnetism.

Next, we shall formulate this condition in a fuller form, but first we introduce the concept of parity of antiferromagnetic structures with respect to some element of the crystallochemical lattice symmetry; this will simplify our discussion.

We shall call a given antiferromagnetic structure even with respect to a given symmetry element if the transformation represented by this element interchanges magnetic moments within the same magnetic sublattice. If the transformation produces an interchange of magnetic moments belonging to different magnetic sublattices, the antiferromagnetic structure is known as odd with respect to the symmetry element being considered. Using this parity concept, we can formulate the condition for the existence of weak ferromagnetism (the "parity condition") as follows.

*Weak ferromagnetism is possible only in antiferromagnetic structures that are even with respect to all lattice translations, and with respect to an inversion center if the lattice has such a center.** Hence it follows that:

a) the magnetic and chemical unit cells are identical for antiferromagnetic structures in which weak ferromagnetism can exist;

b) the directions of the magnetic moments at all sites belonging to the same crystallochemical Bravais lattice and at sites symmetrical with respect to an inversion center should be identical.

Therefore, to find antiferromagnetic structures in which weak ferromagnetism can exist, it is necessary to make parallel all the magnetic moments at all lattice sites related by inversion and parallel translation transformations.** We can then have two possibilities: either the magnetic moment configuration is ferromagnetic (with all magnetic atoms having parallel magnetic moments) or one or more antiferromagnetic structures may be possible. In the former case, all the magnetic atoms belong to the same Bravais lattice or to two Bravais lattices related by an inversion center; in such magnetic substances weak ferromagnetism

*We shall stress once again that here and later we mean symmetry elements of the crystallochemical lattice (which are the Fedorov space groups).

**From then on, we can regard the inversion center and the translations as identical symmetry elements, and drop them from our discussion.

is altogether impossible. In the latter case, the rotation and reflection transformations must be considered before one can establish the possibility of the existence of weak ferromagnetism.

2. CONDITIONS IMPOSED BY ROTATION AND REFLECTION TRANSFORMATIONS

As pointed out in Sec. 1 of Chap. IV, the presence of antiferromagnetic ordering, i.e., the existence of a vector $l \neq 0$ leads to the appearance of a spontaneous magnetic moment $m \neq 0$ only if the magnetic energy has terms of the type

$$m_\alpha l_\beta (\alpha, \beta = x, y, z) \quad (5.1)$$

or terms of higher order in l but linear in m . The local vectors $m(r)$ and $l(r)$ transform in exactly the same way as their integral values (4.2) and (4.1),* i.e., m and l always transform as axial vectors except that l can also undergo a change of sign representing even and odd (with respect to a symmetry element) antiferromagnetic structures.

Bearing in mind these transformation properties of m and l , we can construct a table of the magnetic energy invariants permitted by various rotation and reflection transformations and responsible for the weak ferromagnetism of even (+) and odd (-) antiferromagnetic structures (Table 2).

In Table 2, n_z is a symmetry axis (rotation or screw), and n_z is an n -fold inversion axis, and $\sigma_z \equiv 2_z$ is a symmetry plane (mirror or glide). Table 2 lists the invariants linear in m containing l in powers not higher than 3. These invariants are given in the Cartesian system of coordinates, the Z axis of which is parallel to a given symmetry axis or perpendicular to a given symmetry plane. If a given component of m is not listed in a particular row of the table, then weak ferromagnetism along this direction is not allowed by the particular symmetry element.

*This can easily be shown by writing down the relationship between the discrete and continuous descriptions of an antiferromagnet:

$$\mathcal{M} = \int M(r) dr = \sum_i v_i \left(\sum_n \mu_n / v_i \right),$$

$$\mathcal{L} = \int L(r) dr = \sum_{i, v_i \rightarrow 0} v_i \left(\sum_n^+ \mu_n - \sum_n^- \mu_n \right) / v_i.$$

Here, the summation with respect to i denotes the summation over all magnetic unit cells of a crystal, the volume of each of these cells being v_i ; n represents summation over magnetic sites within the same unit cell, and each of the sums Σ^+ and Σ^- is taken only over the magnetic moments for one direction.

Table 2

No.	Symmetry elements	Structure parity	Invariants
1	$2_z, \sigma_z$	$+$	$m_x l_y, m_y l_x, m_x l_x, m_y l_y, m_z l_z^a$
2		$-$	$m_x l_z, m_y l_z, m_z l_x, m_z l_y^a$
3	$3_z, \bar{3}_z$	$+$	$m_x l_y - m_y l_x, m_z (l_x \pm i l_y)^3, (m_x \pm i m_y) (l_x \pm i l_y)^2 l_z$
4		$-$	
5	$4_z, \bar{4}_z$	$+$	$m_x l_y - m_y l_x, (m_x l_y + m_y l_x) (l_x^2 - l_y^2),$ $(m_x l_x - m_y l_y) l_x l_y$
6		$-$	$m_x l_y + m_y l_x, m_x l_x - m_y l_y, m_z l_x l_y l_z, (ml) l_x l_y,$ $m_z l_z (l_x^2 - l_y^2) (m_x l_y - m_y l_x) l_x l_y, (m_x l_y - m_y l_x) \times$ $\times (l_x^2 - l_y^2), (ml) (l_x^2 - l_y^2)$
7	$6_z, \bar{6}_z$	$+$	$m_x l_y - m_y l_x$
8		$-$	$m_z (l_x \pm i l_y)^3, (m_x \pm i m_y) (l_x \pm i l_y)^2 l_z$

^aApart from the listed second-order invariants, there are also fourth-order invariants obtained by multiplying the former by one of the following quantities: l_x^2, l_y^2, l_z^2 and $l_x l_y$.

Some invariants for even antiferromagnetic structures (for example, ml and $m_z l_z$ in rows 3, 5 and 7) are omitted because of the obvious condition that there is always some other symmetry element with respect to which the given antiferromagnetic structure is odd.*

If the actual crystallographic structure of a magnetic substance is known and the "parity condition" is applied, Table 2 can be used very simply to find those antiferromagnetic structures of the substance which allow weak ferromagnetism, as well as the directions of the vector l for which $m \neq 0$. In general, Table 2 must be applied to each symmetry element of a crystal (more exactly, we need consider only the independent symmetry elements). In this way, we determine also the terms in the magnetic Hamiltonian necessary for a quantitative description of weak ferromagnetism.

*Since magnetic atoms occupy crystallographically equivalent sites, then among symmetry elements there is always one which connects sites belonging to different magnetic sublattices.

In using Table 2, we must bear in mind that if magnetic atoms lie on a simple rotation axis or on a simple mirror plane, an antiferromagnetic structure will always be even with respect to these symmetry elements. Moreover, one of the most important results which follow from Table 2 is that all weakly ferromagnetic structures should be *even with respect to a threefold axis* if one exists.

We shall now consider the sufficient conditions for the existence of weak ferromagnetism for each symmetry system, and we shall ultimately establish and systematically present the invariants in the magnetic energy used to describe weak ferromagnetism quantitatively.

In triclinic crystals, weak ferromagnetism is impossible since all lattice sites are either onefold or twofold and are related to an inversion center.

For monoclinic crystals, the "parity condition" is not only the necessary but also the sufficient condition for the existence of weak ferromagnetism. In these crystals, apart from translations and an inversion center, there is only one independent symmetry element—a plane or a twofold axis. Therefore, if, after applying the "parity condition" (i.e., after postulating parallel magnetic moments at all sites related by translations or an inversion center) the magnetic moment configuration still permits antiferromagnetic ordering, then this ordering is unique and the single independent symmetry element links sites with antiparallel magnetic moments.* Consequently, an antiferromagnetic structure is always odd with respect to that symmetry element and the magnetic energy of a monoclinic antiferromagnet with a structure satisfying the "parity condition" always includes invariants listed in row 2 of Table 2. This row gives four independent second-order invariants such that $m \neq 0$ for any direction of the vector l .

We shall consider next orthorhombic crystals. In these, there are three symmetry elements (three mutually perpendicular symmetry planes, or twofold symmetry axes, or two perpendicular planes and one axis parallel to the line of intersection of these planes) apart from translations and an inversion center. Only two of these elements are independent so that the product of any two elements always gives a new element. Therefore, if an antiferromagnetic structure is odd with respect to one symmetry element (which is necessary for the existence of antiferromagnetism) it should be odd also with respect to the second element

*If magnetic atoms in a monoclinic crystal lie on a simple symmetry axis (or plane), this is sufficient proof of the absence of weak ferromagnetism in such a crystal because then an antiferromagnetic structure should be even with respect to all the symmetry elements (to allow weak ferromagnetism), which is impossible.

and even with respect to the third.* However, any such antiferromagnetic structure automatically allows weak ferromagnetism. Let the element with respect to which an antiferromagnetic structure is even be 2_z (or σ_z). This symmetry element allows the two first invariants in the first row of Table 2. However, it is easily seen (using the second row of Table 2 after a suitable cyclic interchange of the coordinate axes) that these expressions are invariant also with respect to the other two symmetry elements: 2_x (or σ_x) and 2_y (or σ_y).

Thus, if an antiferromagnetic structure, even with respect to translations and an inversion center, exists in any orthorhombic crystal, it should exhibit weak ferromagnetism (for a suitable direction of the vector l). Consequently, the "parity condition" is both the necessary and sufficient condition for the existence of weak ferromagnetism.

If magnetic atoms occupy general crystallographic positions,** then the rotation element, with respect to which an antiferromagnetic structure is even, can be any of the three symmetry elements. Consequently, in an orthorhombic crystal there are, in general, three antiferromagnetic structures which allow weak ferromagnetism. The necessary and sufficient conditions formulated above determine these structures in an unambiguous way: first, we must postulate that all magnetic moments are parallel at all sites linked by translation and inversion, and then we shall take in turn the three remaining symmetry elements requiring magnetic moments to be parallel at sites linked by one of them and antiparallel at sites linked by the two other elements.

If magnetic atoms lie on a twofold rotation axis or on a mirror plane, the antiferromagnetic structure cannot be odd with respect to these symmetry elements. Then weak ferromagnetism can exist in only one antiferromagnetic structure, i.e., that structure for which two other symmetry elements transform into self-coincidence the sites with antiparallel magnetic moments (it is sufficient to require that the structure is odd with respect to one of the symmetry elements; it will automatically be odd with respect to the other element).

Finally, when magnetic atoms lie at the points of intersection of rotation axes or on a line of intersection of two mirror planes, weak ferromagnetism is altogether impossible. Then, the general "parity condition" is incompatible with antiferromagnetism

*Only then the parity with respect to a product of two elements is identical with the parity with respect to the third element (which is a product of the first two).

**General positions are not only those lattice sites through which none of the symmetry element passes, but also the positions on screw axes and glide reflection planes. Special positions are those which lie on simple rotation axes or mirror reflection planes.

(because after applying this condition the magnetic moments at all lattice sites become parallel).

Let us assume that the necessary and sufficient conditions for the existence of weak ferromagnetism in an orthorhombic crystal are satisfied and that 2_z (or σ_z) is that symmetry element with respect to which a given antiferromagnetic structure is even. Then, according to Table 2, the terms responsible for weak ferromagnetism in the magnetic Hamiltonian of any orthorhombic crystal can be represented in the form

$$\mathcal{H}_D = d_1 m_x l_y + d_2 m_y l_x + \text{terms of higher order in } l, \quad (5.2)$$

where d_1 and d_2 are phenomenological theoretical parameters. The corresponding expressions for \mathcal{H}_D for those cases when the antiferromagnetic structure is even with respect to 2_x (σ_x) or 2_y (σ_y) are obtained from (5.2) by a cyclic interchange of coordinates (x, y, z).

It is evident from (5.2) that the weak ferromagnetic moment of orthorhombic crystals is not equal to zero if the antiferromagnetic vector l is perpendicular to the symmetry axis (parallel to the symmetry plane) with respect to which the antiferromagnetic structure is even, but $m = 0$ if the vector l is parallel to that symmetry axis (perpendicular to the symmetry plane).

We shall illustrate our discussion of the conditions for the existence of weak ferromagnetism in orthorhombic crystals by dealing with two space groups: D_{2h}^{16} and D_{2h}^{17} (they are denoted by Nos. 61 and 67 in the International Tables for X-Ray Crystallography [107]). Crystals of the D_{2h}^{16} (Pnma) symmetry group have a primitive Bravais lattice with an inversion center, and crystals with the D_{2h}^{17} (Cmcm) symmetry group have a base-centered Bravais lattice, so that the symmetry elements include translation by half a period along a diagonal of one of the faces of the basic rectangular parallelepiped.

The space group D_{2h}^{16} is shown in Fig. 7a. If we place a magnetic atom in a general position d (x, y, z), then the eight symmetry elements of this group ($E, I, \sigma_x, \sigma_y, \sigma_z, 2_x, 2_y, 2_z$) give eight such atoms with the coordinates

$$\begin{aligned} &1 \ (x, y, z); \ 2 \ (\tfrac{1}{2} - x, \tfrac{1}{2} + y, \tfrac{1}{2} + z); \ 3 \ (x, \tfrac{1}{2} - y, z); \\ &4 \ (\tfrac{1}{2} + x, y, \tfrac{1}{2} - z); \ 5 \ (\bar{x}, \bar{y}, \bar{z}); \ 6 \ (\tfrac{1}{2} + x, \tfrac{1}{2} - y, \tfrac{1}{2} - z); \\ &7 \ (\bar{x}, \tfrac{1}{2} + y, \bar{z}); \ 8 \ (\tfrac{1}{2} - x, \bar{y}, \tfrac{1}{2} + z). \end{aligned}$$

The spin moments of these atoms will be denoted by S_i ($i = 1, 2, \dots, 8$).

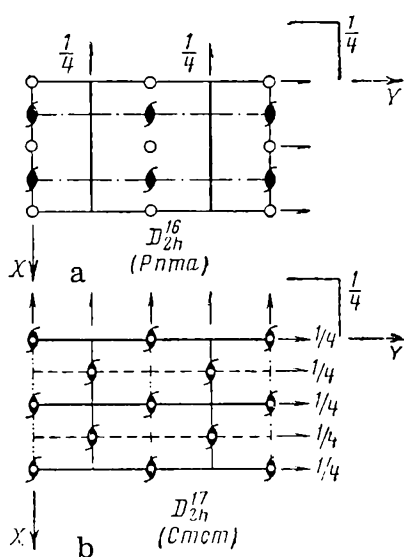


Fig. 7

To find antiferromagnetic structures in which weak ferromagnetism is possible, we should, in accordance with the "parity condition," postulate parallel spins at all sites which transform into self-coincidence by translation over distances that are multiples of the chemical unit cell period. Then, to specify an antiferromagnetic structure, it is sufficient to indicate the directions of the eight spins listed above, and again translations may be regarded as identity symmetry elements. Secondly, we must postulate that spins are parallel at sites related by an inversion center I . Then the whole spin system splits into four groups of parallel (within each group) spins:

$$\text{I. } (S_1 \parallel S_5), \quad \text{II. } (S_2 \parallel S_6), \quad \text{III. } (S_3 \parallel S_7), \quad \text{IV. } (S_4 \parallel S_8). \quad (5.3)$$

After replacing an inversion I with an identity transformation ($I \equiv E$), three symmetry elements remain: σ_x , σ_y , and σ_z (or 2_x , 2_y , and 2_z) of which only two are independent. By making the antiferromagnetic structure even with respect to one and odd with respect to the other two symmetry elements, we obtain three possible antiferromagnetic structures in which weak ferromagnetism may exist.

In particular, the plane σ_x interchanges group I with group II, and III with IV. Consequently, an antiferromagnetic structure that is even with respect to this plane is

$$(S_1 \parallel S_2 \parallel S_5 \parallel S_6) \text{ antiparallel } (S_3 \parallel S_4 \parallel S_7 \parallel S_8) \\ (\text{structure of type } \sigma_x^+),$$

i.e., the spins (1, 2, 5, 6) belong to one magnetic sublattice, and the spins (3, 4, 7, 8) to the other. It is easily seen that the planes σ_y and σ_z interchange spins belonging to different sublattices, and therefore the structure of the σ_x^+ type is odd with respect to these planes. Similarly, we can obtain antiferromagnetic structures which are even with respect to σ_y or σ_z :

$$(S_1 \parallel S_3 \parallel S_5 \parallel S_7) \text{ antiparallel } (S_2 \parallel S_4 \parallel S_6 \parallel S_8) \\ (\text{structure of type } \sigma_y^+);$$

$$(S_1 \parallel S_4 \parallel S_5 \perp S_8) \text{ antiparallel } (S_2 \parallel S_3 \parallel S_6 \parallel S_7) \\ (\text{structure of type } \sigma_z^+).$$

From these structures, we can also derive antiferromagnetic structures permitting weak magnetism if magnetic atoms occupy special crystallographic positions. There are fewer special positions than general positions because several sites which are general positions merge to form one special position. Thus, of the antiferromagnetic structures σ_x^+ , σ_y^+ , and σ_z^+ , only those remain in which special position sites with the same spin directions are brought into coincidence.

The D_{2h}^{16} group has three fourfold special positions [107]. The first two of them (*a* and *b*) coincide with the position of an inversion center with coordinates (000) for the position *a* and coordinates $(00\frac{1}{2})$ for the position *b*. The third position (*c*) lies on the mirror plane σ_y , so that the initial coordinates can be written as $(x\frac{1}{4}z)$.

In making the transition from the general position *d* to the special positions *a* and *b*, points 1, 2, 3, and 4 become coincident with 5, 6, 7, and 8, respectively, i.e., in all three structures only the sites belonging to the same magnetic sublattice become coincident. Consequently, we again obtain three antiferromagnetic structures which now consist not of four pairs of parallel (related by inversion) spins (5.3), but of four individual spins at sites which are inversion centers.

On going over from the general positions *d* (*x y z*) to the special positions *c* ($x\frac{1}{4}z$) the points related by the plane σ_y are brought into coincidence, i.e., 1 with 3, 2 with 4, 5 with 7, and 6 with 8, so that instead of eight sites in a unit cell we have four: I (instead of 1 and 3), II (instead of 5 and 7), III (instead of 2 and 4), and IV (instead of 6 and 8). The only antiferromagnetic structure which permits weak magnetism is thus the structure of the σ_y^+ type, which is even to the given plane σ_y . Since magnetic atoms in the position *c* lie on the σ_y plane, the antiferromagnetic structure is always even with respect to this plane. Together with the requirement of parity with respect to an inversion center, this determines uniquely the only antiferromagnetic structure in which weak ferromagnetism is possible:

$$(S_I \parallel S_{II}) \text{ antiparallel } (S_{III} \perp S_{IV}),$$

which is deduced from the general structure of the σ_y^+ type, if in the latter the spins 1, 2, 5, and 6 are made to coincide with the spins 3, 4, 7, and 8, in the σ_y plane (assuming $y = \frac{1}{4}$).

For the D_{2h}^{17} group, shown in Fig. 7b, we shall consider first only the fourfold positions. There are three types of these positions:

$a(000)$ and $b(0^{1/2}0)$, which are at inversion centers on the σ_x plane; and $c(0y^{1/2})$, which lies at the intersection of the two mirror planes σ_x and σ_z . The complete list of the symmetry elements of this group (with the exception of translations to distances which are multiples of the lattice period) are: E , σ_x , σ_y , σ_z , 2_x , 2_y , 2_z and the products of each of these elements multiplied by a translation $T[1/2, 1/2, 0]$. After replacing the inversion center and this translation with identity transformations ($I \equiv T \equiv E$), we are left with three different symmetry elements, two of which (for example, σ_x and σ_z) are independent. Sites of type c : $(0, y, 1/4)$; $(0, \bar{y}, 3/4)$; $(1/2, y - 1/2, 1/4)$; $(1/2, 1/2 - y, 3/4)$ may be transformed to coincide with one another only by means of translations and an inversion center. Therefore, according to the "parity condition," weak ferromagnetism cannot exist for magnetic atoms for this position. In other words, weak ferromagnetism in the position of c should be absent because the sites for this position are located on the intersection of the mirror planes σ_x and σ_z , and, consequently, there are no symmetry elements with respect to which an antiferromagnetic structure could be odd.

Weak ferromagnetism for each of the positions of the a or b type may exist only for one definite structure which is odd with respect to the σ_z plane. For example, for the b position the coordinates of the sites are as follows:

$$1(0^{1/2}0); 2(1/200); 3(1/20^{1/2}); 4(0^{1/2}1/2).$$

For weak ferromagnetism to exist, the sites related by the translation $T[1/2, 1/2, 0]$, i.e., the sites (1, 2) and (3, 4), must have spins parallel in pairs, and the sites related by the plane σ_z , i.e., (1, 4) and (2, 3), should have antiparallel spins. Consequently, the required antiferromagnetic structure is:

$$(S_1 \parallel S_2) \text{ antiparallel } (S_3 \parallel S_4).$$

We shall now deal with uniaxial crystals characterized by a special principal axis (which may be three-, four- or sixfold).

We shall consider first the tetragonal system. All the crystallographic space groups which belong to this system (from No. 75 to No. 142) may be divided into two types: the first type includes groups of Nos. 75-80 and 93-100, and the second includes all the other groups (Nos. 81-92 and 101-142). In all groups of the first type, the replacement of translations and an inversion center with an identity element leaves only one independent symmetry element: a fourfold axis (rotation, screw, or inversion). In groups of the second type, apart from this fourfold axis, there is one more

symmetry element: a vertical diagonal symmetry plane σ_d (mirror or glide) or a twofold axis 2_d (rotation or screw).*

If an antiferromagnetic structure of a tetragonal crystal whose symmetry is described by a group of the first type is even with respect to a fourfold axis, weak ferromagnetism cannot exist since the antiferromagnetic structure would be odd with respect to an inversion center or translations. For an antiferromagnetic structure which is odd with respect to a fourfold axis, weak ferromagnetism is always possible provided the "parity condition" is satisfied and the magnetic Hamiltonian contains all the invariants of row 6 of Table 2.

In the case of tetragonal crystals of the second type, we have three possibilities corresponding to the three possible combinations of the antiferromagnetic structure parity with respect to the independent symmetry elements 4_z and σ_d (2_d) ($++$, $-+$, $- -$).

If an antiferromagnetic structure is even with respect to 4_z , then it is necessarily odd with respect to σ_d (2_d). Using Table 2, it is easily seen that in this case there may exist weak ferromagnetism described by invariants of the type

$$m_x l_y - m_y l_x, (m_x l_y + m_y l_x) (l_x^2 - l_y^2), (m_x l_x - m_y l_y) l_x l_y \text{ and so on.}^{**} \quad (5.4)$$

If an antiferromagnetic structure is odd with respect to 4_z , it may be even or odd with respect to σ_d (2_d). In the even case, we may have weak ferromagnetism, represented by the following invariants from Table 2 (row 6):

$$m_x l_y + m_y l_x, \quad m_z l_x l_y l_z, \quad (ml) l_x l_y, \\ (m_x l_y - m_y l_x) (l_x^2 - l_y^2) \text{ and others.} \quad (5.5)$$

In the odd case, weak ferromagnetism is due to invariants of the type

$$m_x l_x - m_y l_y, m_z l_z (l_x^2 - l_y^2), (ml) (l_x^2 - l_y^2), (m_x l_y - m_y l_x) l_x l_y \\ \text{and others.} \quad (5.6)$$

We note that if, in a crystal of the second type, the magnetic atoms occupy general positions, then we can have all three cases. The corresponding three antiferromagnetic structures [with weak

*The plane σ_d is perpendicular to the basal plane and parallel to the basal square diagonal, and the axis 2_d lies in the basal plane parallel to the diagonal of the basal square.

**This is not a complete list of all invariants obtained by simple multiplication of lower invariants responsible for weak ferromagnetism by invariants responsible for the usual anisotropy of an antiferromagnet, which consist only of the components of l .

ferromagnetism given by the invariants in (5.4), (5.5), and (5.6)] may be obtained unambiguously if, after applying the "parity condition," the spins are oriented so that one of the three parity combinations listed above is realized with respect to 4_z and $\sigma_d(2_d)$.

In tetragonal crystals there are four types of special position with the following distribution of sites: α) at an inversion center I or on a vertical twofold rotation axis 2_z ,* or on a mirror plane σ_z which is the product of 2_z and I ; β) on a fourfold rotation axis 4_z ; γ) on a diagonal mirror plane σ_d or a rotation axis 2_d ; δ) on a mirror plane σ_x (σ_y) or a rotation axis 2_x (2_y), obtained from the diagonal planes σ_d or the axes 2_d by multiplying them by the fourfold axis 4_z (rotation or screw).

In the case of positions of the α type, there are three possible antiferromagnetic structures with weak ferromagnetism, just as in the case of general positions.

For each of the remaining three types of special position (β , γ , and δ) one of the combinations of parities with respect to 4_z and σ_d (2_d) is always realized: $(+ -)$ for β positions, $(- +)$ for γ positions and $(- -)$ for δ positions. Therefore, for each of those positions there is only one antiferromagnetic structure with weak ferromagnetism, described by invariants of the (5.4), (5.5), or (5.6), respectively.

Weak ferromagnetism cannot exist at all in a tetragonal crystal if the magnetic atom positions belong to at least two of the three position types (β , γ and δ) since any two combinations of parities corresponding to these positions are mutually exclusive. For example, weak ferromagnetism is absent when magnetic atoms lie simultaneously on 4_z and σ_d , since in this case their positions belong to type β as well as to type γ . In other words, for weak ferromagnetism to exist, an antiferromagnetic structure must be even with respect to all symmetry elements, which is impossible (because then we have not antiferromagnetism but the normal ferromagnetism with parallel spins).

We shall consider two special positions of the space group D_{4h}^{14} , shown in Fig. 8 (group No. 135 in the International Tables [107]). We shall assume that, for example, the magnetic atoms occupy an eightfold position i on a mirror plane σ_z :

$$\begin{aligned} &1 (x, y, 0); 2 (1/2 - y, 1/2 + x, 1/2); 3 (y, x, 0); \\ (i) \quad &4 (1/2 + x, 1/2 - y, 1/2); 5 (\bar{x}, \bar{y}, 0); 6 (1/2 + y, 1/2 - x, 1/2); \\ &7 (\bar{y}, \bar{x}, 0); 8 (1/2 - x, 1/2 + y, 1/2). \end{aligned}$$

*This is the symmetry element derived from a fourfold axis: $2_z = 4_z^2$, translated by half a period along an edge of the basal square. An antiferromagnetic structure can never be odd with respect to the 2_z axis.

This position belongs to α type positions which permit three antiferromagnetic structures with weak ferromagnetism. We shall now find these structures. From the "parity conditions," we have

$$S_1 \parallel S_5, S_2 \parallel S_6, S_3 \parallel S_7, S_4 \parallel S_8.$$

Next, we find, using the three possible combinations of parities with respect to 4_z and σ_d ,

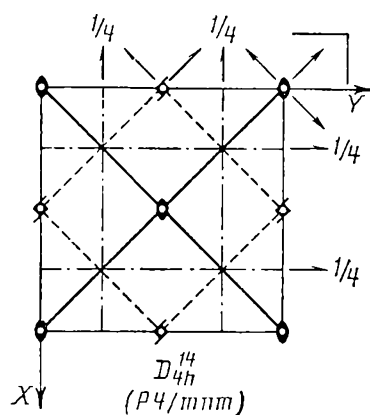


Fig. 8

- (+ -): ($S_1 \parallel S_5$, $S_2 \parallel S_6$) antiparallel ($S_3 \parallel S_7$, $S_4 \parallel S_8$);
 (- +): ($S_1 \parallel S_5$, $S_3 \parallel S_7$) antiparallel ($S_2 \parallel S_6$, $S_4 \parallel S_8$);
 (- -): ($S_1 \parallel S_5$, $S_4 \parallel S_8$) antiparallel ($S_2 \parallel S_6$, $S_3 \parallel S_7$).

Weak ferromagnetism of these structures is described by the invariants (5.4), (5.5), and (5.6), respectively. We shall assume next that the magnetic atoms now occupy the twofold position a lying at an inversion center on a plane σ_d :

$$(a): 1 (0, 0, 0); 2 (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}).$$

This position belongs to type γ , and the weak ferromagnetism for the only antiferromagnetic structure which has S_1 antiparallel to S_2 is given by invariants of the (5.5) type.

We note that magnetic ions in fluorides of divalent transition metals of the iron group (NiF_2 , MnF_2 , etc.) occupy the position a in the D_{4h}^{14} group.

Before considering trigonal and hexagonal crystals we must note the following point. In crystals of these systems (as well as in cubic crystals, discussed below) a threefold symmetry axis is of special importance: any antiferromagnetic structure in which weak ferromagnetism may exist must always be even with respect to this axis. Therefore, to find antiferromagnetic structures with weak ferromagnetism in trigonal and hexagonal crystals we must postulate parallel spins at all sites related not only by translations and inversion centers but also by all threefold axes. If the spin configuration obtained in this way still permits the establishment of an antiferromagnetic structure, then this structure may be weakly ferromagnetic. It is easily seen that this is impossible for all threefold positions and for some sixfold positions, if the doubling of the multiplicity of the latter compared with the former is due to the presence of an inversion center.

After eliminating translations and inversion centers in trigonal crystals, we are again left with either one or two independent symmetry elements. In the former case (groups Nos. 143-146 and 160-161) the only independent symmetry element is a threefold axis 3_z (rotation or screw) and weak ferromagnetism is impossible. In the latter case (groups Nos. 147-159 and 162-167) there is, in addition to the 3_z axis, a vertical diagonal symmetry plane σ_d (σ_x or σ_y) or a horizontal diagonal twofold axis 2_d (2_x or 2_y).^{*} The only possibility of the existence of weak ferromagnetism is when the 3_z axis is even and the σ_d plane (2_d axis) is odd. Therefore, if we want to find an antiferromagnetic structure with weak ferromagnetism in a trigonal crystal, we must make parallel the spins at sites brought into self-coincidence by translations, an inversion center, and the threefold axis 3_z , and then make antiparallel the spins at sites related by the σ_d plane (or the 2_d axis). Weak ferromagnetism is impossible even in the presence of two independent symmetry elements if the σ_d plane (or the 2_d axis) cannot be odd (this will apply if the plane is a mirror one and the magnetic atoms occupy special positions on this plane).

We shall now write the invariants responsible for weak ferromagnetism in trigonal crystals. Bearing in mind that 3_z is an even symmetry element and σ_d (2_d) an odd element, we find from Table 2 one second-order invariant

$$m_x l_y - m_y l_x, \quad (5.7)$$

and two fourth-order invariants

$$m_z [(l_x + i l_y)^3 + (l_x - i l_y)^3], \quad (5.8)$$

$$[(m_x + i m_y) (l_x + i l_y)^2 + (m_x - i m_y) (l_x - i l_y)^2] l_z,$$

or

$$i m_z [(l_x + i l_y)^3 - (l_x - i l_y)^3], \quad (5.9)$$

$$i [(m_x + i m_y) (l_x + i l_y)^2 - (m_x - i m_y) (l_x - i l_y)^2] l_z$$

for $\sigma_d \equiv \sigma_x$ ($2_d \equiv 2_x$) or $\sigma_d \equiv \sigma_y$ ($2_d \equiv 2_y$), respectively.

As an example, we shall consider a trigonal (rhombohedral) crystal with the space group D_{3d}^6 (or $R\bar{3}c$, No. 67, cf. Fig. 9). We

^{*}The plane σ_d is perpendicular and the axis 2_d is parallel to one of the diagonals of the basal rhombus (see, for example, Fig. 9). If these diagonals are the X and Y axes of a Cartesian system of coordinates, then $\sigma_d \equiv \sigma_x$ or σ_y , and $2_d \equiv 2_x$ or 2_y .

shall assume that the magnetic atoms occupy special positions on the 3_z axis; these positions are fourfold for an arbitrary value of the coordinate z (position c):*

(c): 1 $(0, 0, z)$; 2 $(0, 0, \bar{z})$; 3 $(0, 0, \frac{1}{2} + z)$; 4 $(0, 0, \frac{1}{2} - z)$ and twofold if $z = 0$ or $\frac{1}{4}$ (positions a and b):

(a): 1 $(0, 0, 0)$; 2 $(0, 0, \frac{1}{2})$,

(b): 1 $(0, 0, \frac{1}{4})$; 2 $(0, 0, \frac{3}{4})$.

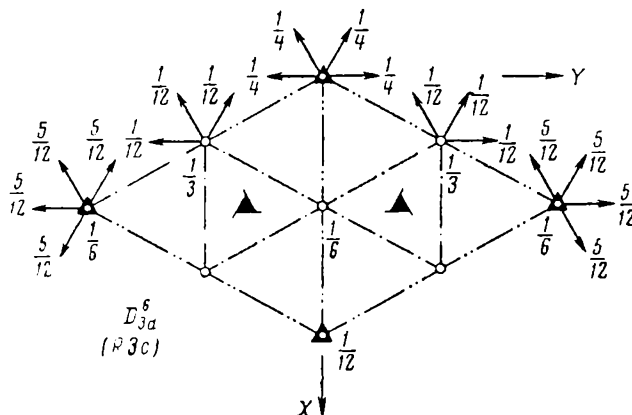


Fig. 9

According to the "parity condition," an antiferromagnetic structure exhibiting weak ferromagnetism for atoms in the c position should be such that the sites related by an inversion center have parallel magnetic moments, i.e.,

$$(S_1 \parallel S_2) \text{ antiparallel } (S_3 \parallel S_4).$$

Since, in this case, $\sigma_d \equiv \sigma_y$ (and $2_d \equiv 2_y$), the invariants which describe weak ferromagnetism of all three positions are (5.7) and (5.9). The symmetry of the D_{3d}^6 group is exhibited by antiferromagnetic crystals with the α - Fe_2O_3 structure (position c) and by transition metal carbonates: MnCO_3 , CoCO_3 , etc. (position a).

We shall now consider hexagonal crystals. Hexagonal space groups having, after the elimination of translations and an inversion center, a single independent symmetry element which is a six-fold axis 6_z (groups Nos. 168-173, 178, 179, 190) can exhibit weak ferromagnetism only in an antiferromagnetic structure which is odd with respect to this axis.

*Contrary to the International Tables [107], we have used an inversion center as the origin of coordinates.

This structure is determined uniquely by applying the "parity condition" to a threefold axis and making antiparallel the spins at sites related via the 6_z axis. The corresponding invariants are given in row 8 of Table 2 [actual combinations of the (5.8) and (5.9) type are made up from these invariants].

Apart from the sixfold axis, hexagonal crystals may have one more independent symmetry element (groups Nos. 174-177, 180-189, and 191-194). This again may be a vertical diagonal plane σ_d (σ_x or σ_y) or a twofold axis 2_d (2_x or 2_y) parallel to the diagonal in the basal rhombus. For general positions of magnetic atoms for which all three combinations of the parities with respect to 6_z and σ_d (2_d) are possible (+ -, - +, --), we can again obtain three antiferromagnetic structures with weak ferromagnetism. For a structure which is even with respect to the 6_z axis, weak ferromagnetism is described by the invariants of (5.7). The invariants of the (5.9) or (5.8) type are responsible for weak antiferromagnetism of an antiferromagnetic structure which is odd with respect to the 6_z axis, the actual invariants to be used depending on whether this structure is even with respect to $\sigma_d \equiv \sigma_x$ ($2_d \equiv 2_x$) or with respect to $\sigma_d \equiv \sigma_y$ ($2_d \equiv 2_y$).

Compounds with the nickel arsenide (NiAs) structure are typical examples of antiferromagnetic crystals of hexagonal symmetry. The space group for this structure is D_{6h}^4 ($P6_3/mmc$, No. 189) in which the magnetic ions occupy a twofold position a at the point of intersection of the axes 6_z and 2_x , which is also an inversion center (Fig. 10, which for the sake of simplicity shows only some of the symmetry elements):

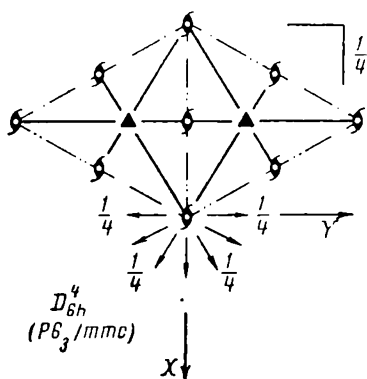


Fig. 10

(a): 1 (0, 0, 0); 2 (0, 0, $\frac{1}{2}$).

For this position, the magnetic ions may have a unique antiferromagnetic structure:

$$S_1 \text{ antiparallel } S_2,$$

which is always even with respect to the rotation axis 2_x and odd with respect to the screw axis 6_z .

It follows that weak ferromagnetism, described by the invariants of the (5.9) type, is possible in this structure.

Finally, we shall consider cubic crystals. We shall discuss first cubic classes T and T_h (space groups Nos. 195-206 [107]). It is easily shown that crystals described by these groups cannot have an antiferromagnetic structure (collinear or weakly non-collinear) which would simultaneously be even with respect to translations, an inversion center (if such a center exists) and

all threefold axes. A threefold axis of these crystals may be regarded as one of the generating elements of symmetry (with respect to this axis, the structure should always be even); a two-fold axis (or a plane) may be used as the other generating element (with respect to which the structure should always be odd). However, the product of the axis 3^+ , directed along a body diagonal of a cube, and of the axis 2^- , directed along a cube edge, gives again a threefold axis with respect to which the structure should be odd, which is impossible. Thus, weak ferromagnetism cannot exist at all in cubic crystals of T and T_h classes.

The situation is different in the case of cubic classes T_d , O and O_h (space groups Nos. 207-230). For these classes, the second generating symmetry element (again in conjunction with a threefold axis) may be a fourfold axis (rotation, screw, or inversion), with respect to which the structure may be odd—which is not self-contradictory. The product of the 3^+ axis, again directed along a body diagonal of the cube, and the 4^- axis, directed along a cube edge, gives in this case a twofold axis (a symmetry plane) which is parallel (perpendicular) to a face diagonal of the cube. Thus the combination of the symmetry elements 3^+4^- satisfies all the necessary “parity conditions” and consequently weak ferromagnetism should exist. These symmetry elements permit one “weakly ferromagnetic” fourth-order invariant:

$$m_x l_x (l_y^2 - l_z^2) + m_y l_y (l_z^2 - l_x^2) + m_z l_z (l_x^2 - l_y^2).$$

It must be stressed that our discussion has been concerned with weak ferromagnetism due to relativistic forces in an antiferromagnet when the initial unperturbed magnetic structure is collinear. Exchange forces may of themselves give rise to noncollinear antiferromagnetic configurations of magnetic moments in a crystal. Then the magnetic energy can no longer be expressed as a function of only two vectors m and l , and, consequently, the above discussion is then inapplicable.

Dzyaloshinskiy [108] and Naish [109] have investigated cubic crystals of UO_2 and Cu_2O structure whose original antiferromagnetic structure was noncollinear and found that the relativistic forces might distort the structure in which weak ferromagnetism was possible. In these cases, four magnetic sublattices are needed to describe the magnetic structure. UO_2 is a representative example of a crystal with this magnetic structure [110].

3. SUMMARY TABLE OF WEAKLY FERROMAGNETIC STRUCTURES

In summarizing the necessary and sufficient conditions for the existence of weak ferromagnetism in antiferromagnetic crystals

with collinear or shortly noncollinear magnetic structures, we can draw the following general conclusions:

1. Weak ferromagnetism of this type should be absent in crystals of triclinic symmetry and in crystals of T and T_h classes of crystal symmetry.

2. In all remaining crystal classes, the "parity condition" is not only the necessary but, in principle, the sufficient condition for the existence of weak ferromagnetism in any antiferromagnetic structure satisfying this "parity condition."*

3. From the point of view of symmetry, weak ferromagnetism should not be a rare phenomenon. On the contrary, the absence of weak ferromagnetism should be the exception (if we ignore triclinic and cubic crystals) since weak ferromagnetism cannot exist only in those cases when magnetic atoms occupy certain special positions in a crystal.

4. In order to find antiferromagnetic structures with weak ferromagnetism in any actual crystal, it is necessary to create magnetic moments at all crystal lattice sites related to one another by translations, an inversion center, or threefold symmetry axes if the lattice has these elements. Then we can have one of three possibilities listed below.

First, if the magnetic moments are parallel at all lattice sites, then and only then are there no antiferromagnetic structures with weak ferromagnetism.

Second, all magnetic sites may belong to two equal groups with magnetic moments parallel within each group; then we have a unique antiferromagnetic structure with weak ferromagnetism for which these two groups of sites represent the two magnetic sublattices of an antiferromagnet.

Third, the application of the "parity condition" to translations, an inversion center, and a threefold axis may divide the whole system of magnetic sites into four equal groups with magnetic moments parallel in each group (four magnetic sublattices). Three possible mutual orientations of magnetic moments in the four magnetic sublattices (assuming that the total magnetic moment is zero) correspond to three different antiferromagnetic structures allowing weak ferromagnetism

$$\left(\begin{smallmatrix} 1 \\ + \end{smallmatrix} \begin{smallmatrix} 2 \\ + \end{smallmatrix} \begin{smallmatrix} 3 \\ - \end{smallmatrix} \begin{smallmatrix} 4 \\ - \end{smallmatrix}, \begin{smallmatrix} 1 \\ + \end{smallmatrix} \begin{smallmatrix} 2 \\ - \end{smallmatrix} \begin{smallmatrix} 3 \\ + \end{smallmatrix} \begin{smallmatrix} 4 \\ - \end{smallmatrix} \text{ and } \begin{smallmatrix} 1 \\ + \end{smallmatrix} \begin{smallmatrix} 2 \\ - \end{smallmatrix} \begin{smallmatrix} 3 \\ - \end{smallmatrix} \begin{smallmatrix} 4 \\ + \end{smallmatrix} \right).$$

*For certain directions of the vector l , the spontaneous magnetic moment m in an antiferromagnetic crystal whose symmetry permits weak ferromagnetism may be found to be zero (for example $m = 0$ for all uniaxial antiferromagnets when the vector l is parallel to the principal crystal axis). However, the presence of weak ferromagnetism terms in the expression for the magnetic energy affects the properties of antiferromagnets even if $m = 0$.

Table 3

No.	System	Nos. of space groups	Parity of structure with respect to independent elements	Invariants
1	Mono-clinic	3—15	2_z^-	$m_x l_z, m_y l_z, m_z l_x, m_z l_y$
2	Ortho-rhombic	16—74	$2_z^+, 2_x^-$	$m_x l_y, m_y l_x$
3			$2_z^-, 2_x^+$	$m_y l_z, m_z l_y$
4			$2_z^-, 2_x^-$	$m_x l_z, m_z l_x$
5	Tetrag-onal	81—92, 101—142	4_z^-	$m_x l_y + m_y l_x, m_x l_x - m_y l_y$
6			$4_z^+, 2_d^-$	$m_x l_y - m_y l_x$
7			$4_z^-, 2_d^+$	$m_x l_y + m_y l_x$
8			$4_z^-, 2_d^-$	$m_x l_x - m_y l_y$
9	Trigonal	147—159, 162—167	$3_z^+, 2_x^-$	$m_x l_y - m_y l_x'$
10			$3_z^+, 2_y^-$	$m_x l_y - m_y l_x$
11	Hexag-onal	168—173, 178, 179, 190	6_z^-	$m_z(l_x \pm il_y)^3, (m_x \pm im_y)(l_x \pm il_y)^2 l_z$
12		174—177, 180—189, 191—194	$6_z^+, 2_x^-$	$m_x l_y - m_y l_x$
13			$6_z^-, 2_x^+$	$im_z[(l_x + il_y)^3 - (l_x - il_y)^3] + i[(m_x + im_y)(l_x + il_y)^2 - (m_x - im_y)(l_x - il_y)^2] l_z$
14			$6_z^-, 2_y^+$	$m_z[(l_x + il_y)^3 + (l_x - il_y)^3] + [(m_x + im_y)(l_x + il_y)^2 + (m_x - im_y)(l_x - il_y)^2] l_z$
15	Cubic	207—230	$4^-, 3^+$	$m_x l_x(l_y^2 - l_z^2) + m_y l_y(l_z^2 - l_x^2) + m_z l_z(l_x^2 - l_y^2)$

Notation. n_α (where $\alpha = x, y, z$) is an n -fold symmetry axis (rotation, screw, or inversion). In particular, 2_α denotes also a symmetry plane (mirror or glide) because $2_\alpha \equiv \sigma_\alpha$. The coordinate axes X and Y in tetragonal crystals are directed along sides of the basal square, and in trigonal and hexagonal crystals they are directed along the short and long diagonals respectively of the basal rhombus. The Z axis in uniaxial crystals is parallel to the principal crystal axis. The indices + and - denote, respectively, the even and odd antiferromagnetic structures.

5. The results of our discussion are summarized in Table 3, which presents a complete classification of all possible cases of weak ferromagnetism and lists the principal invariants which give quantitative descriptions of this ferromagnetism. In order not to overcrowd the table, we give only the lowest-order invariants for each case. Some of the higher-order invariants have been mentioned in the text or may be obtained in Table 2.

According to Table 3, a total of 15 types of antiferromagnetic structure with weak ferromagnetism may exist in the various crystal systems; each type of such structure has its own set of invariants in the magnetic energy expression.*

If the antiferromagnetic structure of an actual crystal is known, we must establish first whether this structure allows weak ferromagnetism at all by applying the "parity condition" to translations, an inversion center, and a threefold axis. Then we can determine the parity of this structure with respect to the independent symmetry elements listed in Table 3, and thus we can find the type of structure from this table.

If the antiferromagnetic structure is not known but the crystallographic space group and the magnetic atom positions are, then, using Table 3, we can again very simply find the antiferromagnetic structures in which weak antiferromagnetism may exist, as well as the invariants which describe this antiferromagnetism. For this purpose, all that is necessary (after applying the "parity condition" to translations, an inversion center, and a threefold axis) is to obtain, in accordance with Table 3, all possible combinations of parities with respect to the independent symmetry elements. In other words, it is necessary to render parallel the magnetic moments at sites related by a symmetry element with the index +, and render antiparallel the magnetic moments at sites related by a symmetry element with the index -. Adding the appropriate invariants from Table 3 to the general part of the Hamiltonian (or the free energy of a given symmetry system) used in Chap. IV to deal with compensated antiferromagnetism, we may investigate the actual properties of each antiferromagnetic structure which allows weak ferromagnetism.

4. THE g -FACTOR ANISOTROPY AND WEAK FERROMAGNETISM

The invariants listed in Table 3 may be regarded as additional terms either in the free energy (when the m and l represent average

*Sometimes the difference between two types of weakly ferromagnetic structure appears only in higher-order invariants, which are not listed in Table 3.

thermodynamic quantities) or in the magnetic Hamiltonian (when m and l represent local distributions of the magnetic moments in a crystal). In both cases, the use of these invariants allows us to investigate, strictly speaking, only the static properties of antiferromagnets exhibiting weak ferromagnetism, such as the stability of various antiferromagnetic states and the magnetization curves in a steady magnetic field. Because of the existence of the gyro-magnetic effect, any discussion of the dynamic properties of magnetic crystals based on the solution of the equations of motion for magnetic moments requires—apart from the Hamiltonian—a knowledge of the coupling of the magnetic moments of the sublattices to the angular momenta. In general, the coupling is of the tensor type

$$M_\alpha = \mu_B g_{\alpha\beta} I_\beta,$$

where M is the magnetic moment and I is the related angular momentum (the latter in units of \hbar), μ_B is the Bohr magneton, and $g_{\alpha\beta}$ is a dimensionless gyromagnetic tensor. The symmetry of this tensor is determined by the crystal symmetry.

In general, we must introduce as many $g_{\alpha\beta}$ tensors as there are Bravais lattices in the crystal, and the relationships between the components of these tensors are governed by the symmetry elements which transform one Bravais lattice into another. The magnetic properties of collinear and slightly noncollinear antiferromagnetic structures may be described by means of two magnetic sublattices. In this connection, we can introduce two effective gyromagnetic tensors $g_{\alpha\beta}^{(1)}$ and $g_{\alpha\beta}^{(2)}$ which are not independent: the relationships between their components are governed by the symmetry elements which relate the angles of these magnetic sublattices.

To determine the form of the tensors $g_{\alpha\beta}^{(1)}$ and $g_{\alpha\beta}^{(2)}$, it is necessary to calculate a scalar of the form*

$$G = g_{\alpha\beta}^{(1)} M_{1\alpha} I_{1\beta} + g_{\alpha\beta}^{(2)} M_{2\alpha} I_{2\beta}.$$

Making this expression invariant with respect to the independent symmetry elements listed in Table 3, we can find explicitly the form of the tensors $g_{\alpha\beta}^{(1)}$ and $g_{\alpha\beta}^{(2)}$ for each of the 15 types of antiferromagnetic structure in which weak antiferromagnetism may exist. All that one has to remember is that the symmetry elements with the index + transform M_j and I_j according to the rules for a normal axial vector, and the symmetry elements with the index -

*It is easily seen that $\mu_B G = M_1^2 + M_2^2$.

represent the same transformation plus an interchange of the subscripts 1 and 2 of these vectors (because they transform one magnetic sublattice into the other).

The g tensors obtained in this way for all the 15 antiferromagnetic structures are listed in Table 4.

In developing the spin-wave theory of compensated antiferromagnetism, we imposed the condition (4.6) of constancy and isotropy of the moduli of the local sublattice magnetization vectors $M_1(\mathbf{r})$ and $M_2(\mathbf{r})$. If we retain this condition here, then weak ferromagnetism in antiferromagnets may appear only as the result of a perturbation in the collinearity of the magnetic moments of the sublattices in such a way that $\mathbf{m} \perp \mathbf{l}$ (the "transverse" weak ferromagnetism). However, we then lose the other possibility, that of an uncompensated magnetic moment appearing due to the departure from strict equality of the moduli of the magnetic moments of the sublattices (the "longitudinal" weak ferromagnetism). The latter effect may be related to the anisotropy of the g factor and we cannot, in general, neglect it by comparison with the non-collinearity effect. We note that in Sec. 1-3 of the present chapter, the condition (4.6) was not used, and therefore the necessary and sufficient conditions for the existence of weak ferromagnetism and Table 3 apply to both effects.

Antiferromagnetism is above all due to the ordering of the angular (spin) momentum of electrons, atoms or ions, by exchange (nonmagnetic) forces. Weak ferromagnetism is a consequence of this ordering but appears only under the additional action of magnetic forces that are weak compared with exchange forces. Therefore, it is natural to assume that, instead of condition (4.6), there is a similar relationship for the angular momenta of the sublattices

$$I_1^2(\mathbf{r}) = I_2^2(\mathbf{r}) = \left(\frac{I_0}{2}\right)^2 = \text{const.} \quad (5.10)$$

The above condition permits a change in the magnetic moments of the sublattices due to the g -factor anisotropy. Moreover, the difference between the g tensors of different sublattices* may lead to a difference between the moduli of the local magnetizations of these sublattices for certain directions of the antiferromagnetic axis. Consequently, condition (5.10) allows for transverse and longitudinal weak ferromagnetism. If this condition is accepted, then the vectors \mathbf{m} and \mathbf{l} of Table 3 should be given a different meaning

*The tensors $g_{\alpha\beta}^{(1)}$ and $g_{\alpha\beta}^{(2)}$ transform into one another by symmetry elements which transform the sites of one sublattice into the sites of the other.

Table 4

System and type of structure	$g^{(1)}$		$g^{(2)}$
I. Monoclinic, 2_z^- (No. 1)	$\begin{vmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{vmatrix}$		$\begin{vmatrix} g_{xx} & g_{xy} & -g_{xz} \\ g_{yx} & g_{yy} & -g_{yz} \\ -g_{zx} & -g_{zy} & g_{zz} \end{vmatrix}$
II. Orthorhombic, $2_z^+ 2_x^-$ *	$\begin{vmatrix} g_{xx} & g_{xy} & 0 \\ g_{yx} & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$		$\begin{vmatrix} g_{xx} & -g_{xy} & 0 \\ -g_{yx} & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$
III. Tetragonal, 4_z^- (No. 5)	$\begin{vmatrix} g_{xx} & g_{xy} & 0 \\ g_{yx} & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$		$\begin{vmatrix} g_{yy} & -g_{yx} & 0 \\ -g_{xy} & g_{xx} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$
IV. $\left\{ \begin{array}{l} \text{Tetragonal, } 4_z^+ 2_d^- \text{ (No. 6)} \\ \text{Trigonal, } 3_z^+ 2_x^- \text{ (No. 9),} \\ \quad 3_z^+ 2_y^- \text{ (No. 10)} \\ \text{Hexagonal, } 6_z^+ 2_x^- \\ \quad \text{(No. 12)} \end{array} \right.$	$\begin{vmatrix} g_{\perp} & g_{xy} & 0 \\ -g_{xy} & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$		$\begin{vmatrix} g_{\perp} & -g_{xy} & 0 \\ g_{xy} & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$
	$\begin{vmatrix} g_{\perp} & g_{xy} & 0 \\ g_{xy} & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$		$\begin{vmatrix} g_{\perp} & -g_{xy} & 0 \\ -g_{xy} & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$
	$\begin{vmatrix} g_{\perp} & g_{xy} & 0 \\ g_{xy} & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$		$\begin{vmatrix} g_{\perp} & -g_{xy} & 0 \\ -g_{xy} & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$
	$\begin{vmatrix} g_{\perp} & g_{xy} & 0 \\ g_{xy} & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$		$\begin{vmatrix} g_{\perp} & -g_{xy} & 0 \\ -g_{xy} & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$
Tetragonal, $4_z^- 2_d^+$ (No. 7)**	$\begin{vmatrix} g_{\perp} & g_{xy} & 0 \\ g_{xy} & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$		$\begin{vmatrix} g_{\perp} & -g_{xy} & 0 \\ -g_{xy} & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$
V.			
Tetragonal, $4_z^- 2_d^-$ (No. 8)	$\begin{vmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$		$\begin{vmatrix} g_{yy} & 0 & 0 \\ 0 & g_{xx} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$
VI. Hexagonal, 6_z^- (No. 11)		$\begin{vmatrix} g_{\perp} & g_{xy} & 0 \\ -g_{xy} & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$	
VII. Hexagonal, $6_z^- 2_x^+$ (No. 13), $6_z^- 2_y^+$ (No. 14)		$\begin{vmatrix} g_{\perp} & 0 & 0 \\ 0 & g_{\perp} & 0 \\ 0 & 0 & g_{zz} \end{vmatrix}$	
VIII. Cubic (T_d , 0, 0 _h), $4^- 3^+$ (No. 15)	$g_{\alpha\beta}^{(1)} = g_{\alpha\beta}^{(2)} = g\delta_{\alpha\beta}$		

*The g tensors for two other types ($2_z^- 2_x^+$ and $2_z^- 2_y^+$) of orthorhombic structure are obtained from the listed tensors by cyclic interchange of x , y and z .

**For these structures, the g tensors are transformed into one another by rotating the coordinate system about the Z axis by 45° .

by defining them, in analogy with (4.5), in terms of angular moments and not magnetic moments:

$$m = \frac{I_1 + I_2}{I_0}, \quad l = \frac{I_1 - I_2}{I_0}. \quad (5.11)$$

(Obviously, if the g factor is a scalar, then definitions (4.5) and (5.11) become identical.) Then, by virtue of (5.10), m and l again obey relationships of the type

$$m^2 + l^2 = 1, \quad (ml) = 0. \quad (5.12)$$

It follows from the second condition of (5.12) that several invariants of order higher than 2 (Table 2) vanish.

Using the relationships (5.12), we can arbitrarily distinguish two physical causes of weak ferromagnetism in antiferromagnetic crystals: first, the noncollinearity of the angular momenta of the sublattices, due to the presence of the magnetic anisotropy energy invariants listed in Table 3; second, the g -factor anisotropy.

We shall illustrate this for three types of antiferromagnetic structure: $2_z^+ 2_x^-$, $n_z^+ 2_x^-$ ($n = 3, 4, 6$), and $4_z^- 2_d^+$. Using the explicit form of the g -tensors given in Table 4 for these structures, we can find the total magnetizations of the two sublattices from

$$M_\alpha = \mu_B (g_{\alpha\beta}^{(1)} I_{1\beta} + g_{\alpha\beta}^{(2)} I_{2\beta}). \quad (5.13)$$

For these cases, using (5.11), we find

$$\begin{aligned} 2_z^+ 2_x^-: \quad M_x &= M_0 (g_{xx} m_x + g_{xy} l_y), \\ M_y &= M_0 (g_{yy} m_y + g_{yx} l_x), \\ M_z &= M_0 g_{zz} m_z; \end{aligned} \quad (5.14)$$

$$\begin{aligned} n_z^+ 2_x^-: \quad M_x &= M_0 (g_{\perp} m_x + g_{xy} l_y), \\ M_y &= M_0 (g_{\perp} m_y - g_{xy} l_x), \\ M_z &= M_0 g_{zz} m_z; \end{aligned} \quad (5.15)$$

$$\begin{aligned} 4_z^- 2_d^+: \quad M_x &= M_0 (g_{\perp} m_x + g_{xy} l_y), \\ M_y &= M_0 (g_{\perp} m_y + g_{xy} l_x), \\ M_z &= M_0 g_{zz} m_z. \end{aligned} \quad (5.16)$$

Here $M_0 = \mu_B I_0$.

From these formulas, it is evident that even if the angular momentum is fully compensated ($m = 0$), the magnetic moment M for antiferromagnetic ordering ($l \neq 0$) does not vanish due to the g -factor anisotropy.

On the other hand, due to the noncollinearity of the angular momenta of the sublattices ($m \neq 0$), the magnetic moment also may not vanish even if the g factors are isotropic ($g_{xx} = g_{yy} = g_{\perp}$, $g_{xy} = g_{yx} = 0$).

In antiferromagnetic structures for which Table 3 does not list second-order invariants (structures of the 6_z^- , $6_z^- 2_x^+$ and $6_z^- 2_y^+$ types for hexagonal crystals) weak ferromagnetism can be solely due to the noncollinearity of the angular momenta since the g tensors of both sublattices are then identical.

We shall now consider the actual properties of various types of magnetic structure with weak ferromagnetism.

CHAPTER VI

Weak Ferromagnetism in Uniaxial Crystals of Even Antiferromagnetic Structure with Respect to the Principal Axis

First we shall consider uniaxial crystals, i.e., those crystals which have an axis of symmetry $n_z = 3_z, 4_z,$ or 6_z . It is evident from Table 3 that the spontaneous moment (angular momentum or magnetic moment) is zero for cases when the spontaneous antiferromagnetic axis coincides with the crystal axis n_z . However, if the antiferromagnetic axis lies in the basal plane, a magnetic moment is established in this plane (in some cases a magnetic moment may appear along the n_z axis due to higher-order invariants).

It is convenient to consider separately the group of uniaxial crystals which have the same second-order invariants and the same g tensors. In Table 4, these structures are denoted by IV. They are even with respect to the principal axis n_z and odd with respect to diagonal twofold axes or with respect to symmetry planes.

Following our notation, all these structures will be denoted by a single symbol n^+2^- . From the physical point of view, the distinguishing property of these structures is their transverse weak ferromagnetism. Assuming that the antiferromagnetic vector l lies in the basal plane ($l_z = 0$), it is easily seen from (5.15) that $(Ml) = 0$. Moreover, as we shall see, the spontaneous magnetic moment of the n^+2^- structures is isotropic in the sense that it does not depend on the direction of l in the basal plane.

1. GROUND STATE AND MAGNETIZATION CURVES AT $T = 0^\circ\text{K}$

The total energy density for n^+2^- structures ($n = 3, 4, 6$) is obtained by adding to the energy of a uniaxial antiferromagnet,

given by (4.4), a common invariant (5.7) taken from Table 3, and by allowing for the tensor nature of the g factor in the term containing the external magnetic field. Using (5.12) and (5.15), and including only the terms whose order in m and l is no higher than the second, we find

$$\begin{aligned} \mathcal{H}(\mathbf{r}) = & \frac{A}{2} m^2 + \frac{a}{2} m_z^2 + \frac{b}{2} l_z^2 - d [\mathbf{m} \times \mathbf{l}]_z - \\ & - h_x (m_x + \tau l_y) - h_y (m_y - \tau l_x) - h_z m_z + \mathcal{H}_{\text{inhom}}. \end{aligned} \quad (6.1)$$

Here, $h_x = g_{\alpha x} M_0 H_x$, $\tau = \frac{g_{xy}}{g_{\perp}}$, and $\mathcal{H}_{\text{inhom}}$ is that part of the exchange energy due to the inhomogeneities of m and l and of the same form as in the corresponding expression (4.4) for a normal antiferromagnet. Moreover, we are neglecting the magnetostatic energy since we shall consider only weak magnetizations $M \ll M_0$. The parameter d represents a constant, a quantitative characteristic of the specific magnetic anisotropy energy, responsible, as shown below, for the noncollinearity of the angular momenta of the sublattices. The order of the parameter d is the same as that of the other constants a and b , the factors in front of the anisotropic terms containing the squares of m and l .

We shall first assume that $\mathcal{H}_{\text{inhom}} = 0$, and investigate the ground state. To find the conditions for the weakly ferromagnetic state, we shall consider the case $h = 0$. In this case, the ground state energy can be written in the form

$$\begin{aligned} \frac{\mathcal{H}_0}{V} = & \frac{A}{2} m^2 + \frac{a}{2} m^2 \sin^2 \theta \cos^2 \gamma + \\ & + \frac{b}{2} (1 - m^2) \cos^2 \theta + dm \sqrt{1 - m^2} \sin \theta \sin \gamma. \end{aligned} \quad (6.2)$$

Using the conditions (5.12), we change to new independent variables: m is the absolute value of \mathbf{m} , θ is the polar angle of the vector l , and γ is the angle representing the direction of the vector \mathbf{m} in a plane perpendicular to l (i.e. the angle from the line of intersection of this plane with the plane containing the Z axis and the vector l ; (Fig. 11). It is characteristic that \mathcal{H}_0 is independent of the azimuthal angle φ of the vector l . This is due to the fact that we are neglecting, in the Hamiltonian, the terms responsible for the anisotropy in the basal plane.

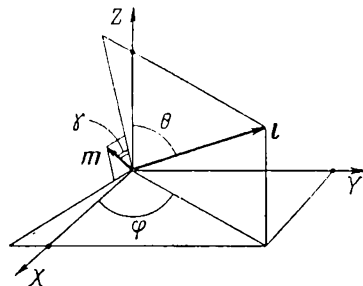


Fig. 11

Minimizing the expression (6.2) with respect to m , θ , and γ , we find the following two possible states:

- I. $\sin \theta = 0$, $m = 0$, $l = 1$ when $b + \frac{d^2}{A} < 0$.
 II. $\cos \theta = 0$, $\cos \gamma = 0$, $l = \sqrt{1 - m^2} \approx 1$, $m \simeq \frac{d}{A}$
 when $b + \frac{d^2}{A} > 0$.

The first state is antiferromagnetic, and the second is weakly ferromagnetic. The spontaneous angular momentum m of state II is perpendicular to the Z axis (like the antiferromagnetic vector l). Its value is determined by the ratio of the second-order anisotropy constant d and the exchange interaction constant A , which is usually of the order of 10^{-2} – 10^{-5} . This is the value relative to the maximum possible angular momentum l_0 (obtained when the sublattice moments are parallel).

From the angular momentum m , we can find, using (5.15), the related spontaneous magnetic moment:

$$M_s = \sqrt{M_x^2 + M_y^2} = M_0 g_{\perp} (m + \tau l).$$

Using the above solution for m and l , we find

$$M_s \simeq M_0 g_{\perp} \left(\frac{H_D}{H_E} + \tau \right), \quad (6.3)$$

where $H_E = \frac{A}{M_0 g_{\perp}}$ is the effective exchange force field, and $H_D = \frac{d}{M_0 g_{\perp}}$ is the effective magnetic anisotropy field responsible for the noncollinearity of the angular momenta of the magnetic sublattices; to distinguish the latter field from the anisotropy field $H_A = b/M_0 g_{\perp}$, responsible for the orientation of the vector l with respect to the crystallographic axes, we shall call H_D the Dzyaloshinskiy field.

Thus the spontaneous magnetic moment of weak ferromagnets with structures of the n^{+2-} type consists, in general, of two additive terms: one—with a relative contribution d/A —due to the noncollinearity of the angular momenta of the sublattices; the other—with a relative contribution $\tau = \frac{g_{xy}}{g_{\perp}}$ —due to the g -factor anisotropy, which leads to an additional noncollinearity of the magnetic moments of the sublattices. The total magnetic moment (and its separate componets) is perpendicular to the antiferromagnetic axis l and its value is independent of the orientation of this axis in the basal plane.

The order of magnitude of \dot{a}/A has been discussed already. As regards the quantity τ , we may assume that the g -factor anisotropy is due to the same forces which lead to the incomplete "freezing" of the orbital magnetism in ferromagnets and antiferromagnets so that the g factor is not equal to 2.* In that case τ should be of the order of $|g-2|$, which may amount to 0.01 or even 0.1 in some crystals.

The expression (6.3) may be written more simply as follows:

$$M_s = \chi_{\perp} \bar{H}_D, \quad (6.3')$$

where

$$\chi_{\perp} = \frac{M_0 g_{\perp}}{H_E} \quad (6.4)$$

is the normal transverse magnetic susceptibility of an antiferromagnet and

$$\bar{H}_D = H_D + \tau H_E. \quad (6.5)$$

According to (6.4), the spontaneous magnetization in the case of weak ferromagnetism may be regarded as the magnetization of an antiferromagnet due to a transverse internal magnetic field \bar{H}_D .

We shall now consider the behavior of a weak ferromagnet in an external field H . This may be done in a general way using the Hamiltonian (6.1) and independent variables m , γ , θ , and φ . However, the symmetry indicates clearly that in an external field the vector l remains in the basal plane, and therefore to describe the state of a system, it is sufficient to take two independent variables in the form of components of the vector m in the basal plane m_{\perp} and along the crystal axis m_z (Fig. 12). In terms of these variables, the ground-state energy may be written in the form

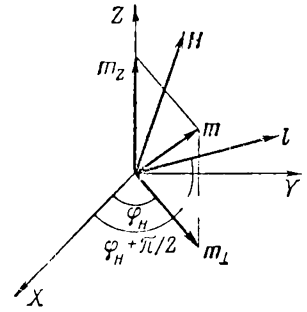


Fig. 12

$$\frac{\mathcal{H}_0}{V} = \frac{A}{2} (m_{\perp}^2 + m_z^2) + \frac{a}{2} m_z^2 - dm_{\perp} l_{\perp} - h_{\perp} (m_{\perp} + \tau l_{\perp}) - h_z m_z, \quad (6.6)$$

where

$$l_{\perp} = \sqrt{1 - m_{\perp}^2 - m_z^2} \quad (l_z = 0). \quad (6.7)$$

*This is due to the spin-orbital interaction which "mixes" various orbital states of a magnetic atom.

From the condition for minimum \mathcal{H}_0 , we find approximately (for $m^2 \ll 1$):

$$m_{\perp} = \frac{d + h_{\perp}}{A + a + \tau h_{\perp}}, \quad m_z = \frac{h_z}{A + a + \tau h_{\perp}}. \quad (6.8)$$

If we use a linear approximation with respect to the external field, the corresponding values of the magnetization become

$$M_{\perp} = M_s + \chi_{\perp} H_{\perp}, \quad M_z = \chi_z H_z, \quad (6.9)$$

where

$$\chi_z = \frac{(g_{zz} M_0)^2}{A + a} \quad (6.10)$$

is the transverse susceptibility along the Z axis. The anisotropy of the transverse susceptibility is now governed not only by the anisotropy constant a , but also by the ratio of the corresponding components of the g tensor:

$$\frac{\chi_{\perp}}{\chi_z} = \left(\frac{g_{\perp}}{g_{zz}} \right)^2 \frac{A + a}{A}.$$

According to the second formula in (6.9), in our approximation weak ferromagnetism cannot affect the magnetization along the Z axis: the spontaneous magnetic moment of weak ferromagnets, in contrast to normal ferromagnets, is not rotated by an external field applied along the hard magnetization axis.

2. SPIN-WAVE SPECTRUM AND TEMPERATURE DEPENDENCE OF MAGNETIZATION

The next step is, as usual, a calculation of the spin-wave spectrum. For this purpose, it is necessary to consider small oscillations of the angular momenta of sublattices $I_1(\mathbf{r})$ and $I_2(\mathbf{r})$ about their equilibrium positions (5.11), (6.7), and (6.8). In a coordinate system for each lattice in which the quantization axis of the momentum I_j (determined by the equilibrium direction of the classical vector I_{j0}) is taken to be the Z_j axis, the operators $I_j(\mathbf{r})$ may be expressed approximately in terms of Bose amplitudes $b_r^{(j)\dagger}$ and $b_r^{(j)}$ [cf. formula (1.15)]:

$$\begin{aligned}
I_{ix_j} &\simeq \sqrt{\frac{I_0}{2}} (b_r^{(j)} + b_r^{\dagger(j)}), \\
I_{iy_j} &\simeq i \sqrt{\frac{I_0}{2}} (b_r^{(j)} - b_r^{\dagger(j)}), \\
I_{iz_j} &= I_0 - b_r^{(j)} b_r^{\dagger(j)}.
\end{aligned} \tag{6.11}$$

If we now transform to a general system of coordinates XYZ related to the crystal axes [this may be done by means of relationships of the (1.18) type] $b_r^{\dagger(j)}$ and $b_r^{(j)}$ may be used to find the vectors m and l from (5.11); consequently, we can obtain the Hamiltonian (6.1).

Selecting from the total Hamiltonian $\mathcal{H} = \int \mathcal{H}(\mathbf{r}) d\mathbf{r}$ the term quadratic in $b_r^{(j)}$ and $b_r^{\dagger(j)}$, and reducing this term to its diagonal form, we again, as for normal antiferromagnets, obtain two spin-wave modes. We shall not give here the details of this calculation because it is completely analogous to the calculation for ferromagnets and antiferromagnets (see, for example, Appendix D).

The approximate expressions for the energy of spin waves in not too strong fields ($h \ll A$) have the following form:

$$\varepsilon_{1k} = \frac{1}{I_0} [A (B_{\perp} k_{\perp}^2 + B_z k_z^2) + h_{\perp} (h_{\perp} + d + \tau A)]^{\frac{1}{2}}, \tag{6.12}$$

$$\varepsilon_{2k} = \frac{1}{I_0} [A (B_{\perp} k_{\perp}^2 + B_z k_z^2) + Ab + d^2 + h_z^2 + h_{\perp} (d + \tau A)]^{\frac{1}{2}}. \tag{6.13}$$

Here we have retained the notation used in Chap. IV [cf. formulas (4.26)].*

We note that, as for normal uniaxial antiferromagnets, one of the modes of the spectrum has a small energy gap which disappears (if we ignore the basal-plane anisotropy) when $H = 0$. The energy gap for the second mode is determined by the average geometric mean of the exchange energy and the magnetic anisotropy energy $\mu_{\perp} H_{EA} \sim \sqrt{Ab}$. The parameter d responsible for weak ferromagnetism makes this gap somewhat larger.

Next, we can calculate the thermodynamic potential of spin waves (4.56), and then the temperature dependence of the spontaneous magnetization and of the magnetic susceptibility [in expressions of the (6.9) type, which remain valid also at $T \neq 0$]. In the temperature range $\mu_{\perp} H_{EA} \ll \kappa T \ll \kappa \Theta_N$, we have

$$M_s(T) = M_s(0) (1 - \eta T^2), \tag{6.14}$$

*With the exception of the quantity h_{\perp} , which now gives the transverse component (with respect to the Z axis) of the external field.

$$\chi_{\perp}(T) = \chi_{\perp}(0) (1 - \eta T^2), \quad (6.15)$$

$$\chi_z(T) = \chi_z(0) (1 - \eta' T^2), \quad (6.16)$$

where

$$\eta \approx \eta' = \frac{A\kappa^2}{48J_{\perp}^2 J_z I_0^2}.$$

At lower temperatures, when $\mu H, \mu H_D \ll \kappa T \ll \mu_{\perp} H_{EA}$, thermal motion may excite only the first spin-wave mode. In formula (6.14), the coefficient η should then be replaced by $\eta/2$, but formula (6.15) remains unaffected and the susceptibility along the Z axis (6.16) becomes independent of temperature.* If a more rigorous calculation is carried out, including in the spin-wave energy ε_{1k} , terms of the order of $AB_k m^2$ and $AA_k m^2$, we obtain, instead of (6.16), the following expression for $\chi_z(T)$ in the temperature range $\kappa T \ll \mu_{\perp} H_{EA}$

$$\chi_z(T) = \chi_z(0) (1 + \zeta T^4),$$

similar to the expression for a normal antiferromagnet in the (z/\perp) state [cf. formula (D.30) in Appendix D; this formula determines the value of the coefficient ζ].

Thus, the spontaneous magnetic moment of weak ferromagnets should vary not according to the $T^{1/2}$ law, typical of normal ferromagnets, but according to the T^2 law. The temperature dependence of the magnetic susceptibility and of the magnetic part of the specific heat C_s is the same as for normal antiferromagnets. It is interesting to find the relationship between C_s and the temperature variation of the spontaneous magnetization. Comparing the formula (6.14) with the corresponding formulas of Chap. IV, we obtain the following general relationship for C_s

$$\frac{C_s}{\chi_{\perp} T} = \frac{16\pi^2}{5} \left(\frac{\kappa}{\mu} \right)^2 \frac{M_s(0) - M_s(T)}{M_s(0)}, \quad (6.17)$$

which is valid both when $\kappa T \gg \mu H_{EA}$ and when $\kappa T \ll \mu H_{EA}$.

3. ROLE OF HIGHER-ORDER ANISOTROPY TERMS

We shall now consider briefly the role of magnetic anisotropy terms of order higher than the second, responsible for the

*The coefficient η is related to the coefficient α , introduced in Sec. 4 of Chap. IV:

$$\frac{1}{4} \alpha = \chi_{\perp}(0) \eta = \frac{(g_{\perp} M_0)^2}{A} \eta.$$

anisotropy of the magnetic properties of a weak ferromagnet in the basal plane. In principle, the influence of these terms has already been dealt with in discussing normal antiferromagnetism: their role reduces to one in which the energy gap (even when $H = 0$) appears in the first mode of the spin-wave spectrum; this gap is determined by the geometric means of the exchange energy and the corresponding magnetic energy of higher-order anisotropy.

Moreover, to ensure that when a magnetic field is rotated in the basal plane, the antiferromagnet vector l rotates with the field and remains perpendicular to it, the field intensity should exceed a certain "threshold" value governed also by this mean energy.

We have shown in Sec. 1 that the expression for the magnetic energy of weak ferromagnets may also contain terms of higher order in l but linear in m .

According to (5.4), for a structure of the $4_z^+ 2_d^-$ type, these terms are invariants of the type

$$(l_x^2 - l_y^2) (m_x l_y + m_y l_x), \quad l_x l_y (m_x l_x - m_y l_y), \quad (6.18)$$

and for structures of the $3_z^+ 2_x^-$ and $3_z^+ 2_y^-$ types, they are, respectively, invariants (5.8) or (5.9). The presence of the (6.18) type terms in the expression for the energy should lead to an anisotropic correction to the spontaneous moment of tetragonal crystals (which would depend on the direction of l in the basal plane). The invariants (5.8) and (5.9) should lead to the appearance of a spontaneous moment along the Z axis direction in trigonal crystals, the magnitude (and even the sign) of this moment depending, on the azimuthal angle φ of the vector l . The maximum values of the moments due to these anisotropic corrections are governed by the ratio of the constant multiplier of the corresponding invariant to the exchange interaction constant A .

As an example, we shall consider in some detail structures of the $3_z^+, 2_y^-$ type exhibited by the weakly ferromagnetic crystals $\alpha\text{-Fe}_2\text{O}_3$ and MnCO_3 . For structures of this type, we must add to the magnetic Hamiltonian (6.1) terms of the following type [108]*

$$\begin{aligned} & \frac{q}{2} [(l_x + i l_y)^3 + (l_x - i l_y)^3] l_z + \frac{i}{2i} [(l_x + i l_y)^3 - (l_x - i l_y)^3] m_z + \\ & + \frac{e}{2} [(l_x + i l_y)^6 + (l_x - i l_y)^6]. \end{aligned} \quad (6.19)$$

*We are not listing here invariants of the l_z^4, l_z^6 , etc. type, which yield no new corrections compared with the second-order invariants in the Hamiltonian (6.1); we are also omitting the second of the invariants in (5.9) because its resultant corrections are unimportant for the states considered here.

From the condition for a minimum \mathcal{H}_0 , we can show that if these terms are allowed for, the state II splits into two new states:

$$\text{II}_1: \theta \approx \frac{\pi}{2} + \frac{q}{b}, \quad \varphi = 0, \quad m_y = \frac{d}{A}, \quad m_x = m_z = 0, \quad (6.20)$$

$$\text{II}_2: \theta = \frac{\pi}{2}, \quad \varphi = \frac{\pi}{2}, \quad m_x = \frac{d}{A}, \quad m_z = \frac{t}{A+a}, \quad m_y = 0. \quad (6.21)$$

The states II_1 and II_2 are obtained if, in addition to the condition

$$Ab + d^2 > 0 \quad (6.22)$$

the following inequality is satisfied.*

$$e < \frac{q^2}{4b} \quad \text{or} \quad e > \frac{q^2}{4b}. \quad (6.23)$$

In the state II, the vector l lies in the σ_y plane, making a small angle $\delta_0 = \frac{q}{b}$ with the basal plane, and the spontaneous moment m is directed along the twofold rotation axis 2_y . In the II_2 state, the vector l is directed along the 2_y axis, and the vector m lies in the σ_y plane, so that in addition to its principal component m_x , related to a second-order invariant, there is also a small component along the Z axis due to the fourth-order invariants.

Let us now assume that a field H making an angle φ_H with the X axis is applied to the basal plane. Then, again minimizing \mathcal{H}_0 , we find that in fields $h_{eq} \ll h \ll$

$$m_{\perp} \parallel H, \quad m_{\perp} = \frac{d+h}{A}, \quad m_z = \frac{t}{A+a} \cos 3\varphi_H, \quad (6.24)$$

and the vector l ($l \approx 1$) lies in a plane perpendicular to H , making with the basal plane an angle

$$\delta = \delta_0 \sin 3\varphi_H. \quad (6.25)$$

The field h_{eq} is the effective magnetic anisotropy field in the

*More rigorously, the inequalities (6.23) should be written

$$e + \frac{l^2}{4(A+a)} < \text{or} > \frac{q^2}{4b}.$$

However, the term l^2 is of higher order compared with other terms.

basal plane; when $h \gg h_{eq}$, we have saturation in the sense that $m_{\perp} \parallel H$. Approximately

$$h_{eq} = \frac{36A |e - q^2/b|}{d + \tau A}. \quad (6.26)$$

Knowing the equilibrium vectors m and l , we can calculate again the spectrum of oscillations of the system near this equilibrium state. We shall give here an expression for the spin-wave energy for $k = 0$ only, since the terms depending on k are of the same form as in (6.12):

$$\varepsilon_{10} = \frac{1}{I_0} \left[h(h + d + \tau A) + 36 \left(e - \frac{q^2}{b} \right) A \cos 6\varphi_H \right]^{1/2}, \quad (6.27)$$

$$\varepsilon_{20} = \frac{1}{I_0} [Ab + d^2 + 9Bq + h(d + \tau A) + 6Be \cos 6\varphi_H]^{1/2}.$$

It is evident from (6.27) that the fourth- and sixth-order anisotropies have practically no influence on the energy of the second mode of the spin waves, because the terms with q and e are always small compared with the term Ab . On the other hand, the basal-plane anisotropy may considerably affect the first mode of the spin waves if the field H is not too high ($h \gtrsim h_{eq}$). The energy gap for the second mode is anisotropic—it depends on the direction of H . These results will be needed later in a discussion of the resonance properties of weak ferromagnets.

In conclusion, it must be pointed out that in the n^{+2-} structures the g factor anisotropy makes no new contribution to the static or dynamic properties of a weak ferromagnet: the effect of an anisotropic g factor reduces to the renormalization of the parameter d by the substitution

$$d \rightarrow \bar{d} = d + \tau A. \quad (6.28)$$

4. DISCUSSION OF EXPERIMENTAL DATA

Experimental investigations of weak ferromagnetism of trigonal (rhombohedral) crystals of α -Fe₂O₃, MnCO₃, CoCO₃, and CrF₃ confirm the main conclusions of the theory. All these weak ferromagnets belong to the $3_2^+ 2_2^-$ type (space group D_{3d}^6).

Neutron-diffraction data [90, 111, 112] show that in all these crystals the magnetic and chemical unit cells are identical. This general condition applies also to all other known weakly ferromagnetic crystals irrespective of their crystal system.

A comparison of the antiferromagnetic structures of a weakly ferromagnetic crystal $\alpha\text{-Fe}_2\text{O}_3$ and a compensated antiferromagnet Cr_2O_3 , which have the same crystallographic structure, shows clearly the role of an inversion center [14]. In $\alpha\text{-Fe}_2\text{O}_3$, the antiferromagnetic structure is even with respect to an inversion center because the Fe^{3+} ions, related by this symmetry element, have parallel magnetic moments (Fig. 13a). In Cr_2O_3 , an inversion center relates the Cr^{3+} ions with antiparallel magnetic moments (Fig. 13b), and consequently weak ferromagnetism cannot exist in this compound even if the vector l lies in the basal plane.*

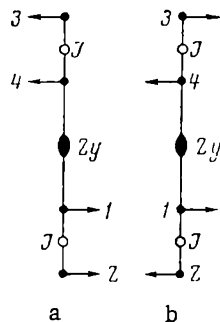


Fig. 13

Using $\alpha\text{-Fe}_2\text{O}_3$ as an example, we can also demonstrate a transition from the antiferromagnetic state to the weakly ferromagnetic state, accompanied by a change in the direction of the vector l [14]. Depending on temperature, this compound may either be in antiferromagnetic state I ($l \parallel Z$) or in one of the weakly ferromagnetic states II₁ (l is approximately parallel to the X axis). The former state is obtained at temperatures $T < 250^\circ\text{K}$, and the latter at higher temperatures up to the Néel point (950°K) [13].**

Neutron-diffraction investigations have established that the antiferromagnetic axes of MnCO_3 [90] and CrF_3 [112] crystals lie near the basal plane. For MnCO_3 , the vector l is, moreover, parallel to the symmetry plane σ_y . In CoCO_3 [90], the antiferromagnetic axis also lies in the symmetry plane σ_y but it makes an angle of $46 \pm 4^\circ$ as with a trigonal axis. Consequently, both these carbonates are in the weakly ferromagnetic state II₁. The fact that in CoCO_3 the vector l deviates from the basal plane by a large angle means that the anisotropy constants b and q are of the same order of magnitude. The noncollinearity of the magnetic moments leading to weak ferromagnetism was first detected, at

*In fact, l is directed along a trigonal axis.

**This transition is accompanied by a change in the sign of the effective anisotropy constant $b' = b + d^2/A$. The direction of the vector l does not change in jumps, but gradually, so that this transition extends over a very wide range of temperatures [113, 114]. This occurs because close to the temperature at which the constant b changes its sign, higher-order terms may be important in the magnetic anisotropy energy, for example, terms such as

$$l_z^4 \text{ and } l_z[(l_x + il_y)^3 + (l_x - il_z)^3].$$

We note that, in accordance with the experimental data, the spontaneous magnetic moment M_s in state I is considerably smaller than in state II₁, but still does not vanish. This is obviously due to various crystal defects and possible ferromagnetic impurities. This conclusion may be drawn from the fact that the value of the magnetic moment in state I is different for samples of different origin and depends strongly on the impurity content.

least qualitatively, in CoCO_3 by neutron-diffraction measurements. In FeCO_3 [90], which is isomorphous with MnCO_3 and CoCO_3 , the vector l is directed along a trigonal axis, i.e., its magnetic state is the state I; other experiments also show that weak ferromagnetism is not present in FeCO_3 .

The spontaneous magnetic moment of all these weakly ferromagnetic crystals lies, in accordance with the theory, in the basal plane; the field dependence of the magnetization is given by (6.9), and remains the same, for any given value of the field, for all directions in the basal plane.

However, the linear dependence of the magnetization—both transverse and longitudinal—on the field is observed only in sufficiently strong fields; for example, in the case of MnCO we must have $H_\perp > 2$ kilooersteds and $H_z > 4$ kilooersteds (Fig. 14 [92]). In the case of transverse magnetization, this is due to various crystal defects and, possibly, due to an antiferromagnetic domain structure. Therefore, it would be interesting to investigate the initial magnetization curves in a transverse field as a function of the previous history of a sample.

In the case of longitudinal magnetization, the initial (nonlinear) part of the magnetization curve $M_z(H)$ is explained by assuming, in accordance with the neutron-diffraction data [90], that the initial state (when $H = 0$) of MnCO_3 is the state II_1 . Then the appearance of the z component of the magnetization (due to an external field H_z) should—due to the presence of the second invariant of (6.19) in the free energy—rotate the

vector l in the basal plane in the direction toward the nearest symmetry axis 2_d . This rotation process makes an additional contribution to the magnetic susceptibility, which vanishes when the vector l becomes parallel to the 2_d axis and the rotation ends. We are dealing here with a forced transition, at the expense of the external-field energy, from the state II_1 to the state II_2 . The calculation for this transition has been given by Borovik-Romanov [92] and we shall not consider it further (see also Chap. VII, Sec. 5).

The temperature dependence of the spontaneous magnetization and magnetic susceptibility of single-crystal trigonal weak ferromagnets has been investigated in detail by Borovik-Romanov

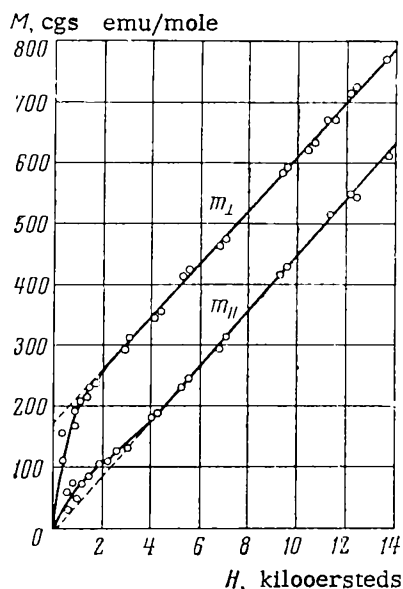


Fig. 14

for manganese carbonate [92], and by Borovik-Romanov and Ozhogin for cobalt carbonate [93]. They have found that the spontaneous magnetization of MnCO_3 in a wide range of temperatures—from 1.3 to 23°K (the latter temperature is 0.7 of the Neel temperature)—decreases in accordance with the theoretical quadratic law (6.14).

In the case of CoCO_3 , the temperature dependence of M_s in the range 5–10°K has been found to obey satisfactorily the quadratic formula (6.14) with a constant coefficient η . On cooling, a change in the nature of the temperature dependence of M_s has been observed near 4.5°K; it may be explained by a halving of coefficient η with the transition from the temperature region $\kappa T \gg \mu H_{EA}$ to the temperature region $\kappa T \ll \mu H_{EA}$. This effect, as well as the analogous change in the multiplier of T^3 in the spin part of the specific heat (Chap. IV), is due to the “decoupling” from the thermal motion of the second mode of the spin waves at sufficiently low temperatures when the thermal energy becomes less than the energy gap of this mode.

The temperature dependence of the magnetic susceptibility of MnCO_3 and CoCO_3 has been found to disagree with the theoretical formulas (6.15) and (6.16), by which χ_{\perp} and χ_z should decrease with increase in temperature in accordance with the same law, and with the same coefficient η , as M_s (if $\kappa T \gg \mu H_{EA}$). In fact, the fall in the magnetic susceptibility has been found to proceed much more slowly, and it is impossible to say whether the quadratic temperature dependence is obeyed at all. The disagreement between the spin-wave theory and experiment is the same as in the temperature dependence of the transverse magnetic susceptibility of normal ferromagnets (Sec. 4, Chap. IV).

Table 5 lists values of the magnetic properties of MnCO_3 , CoCO_3 , and $\alpha\text{-Fe}_2\text{O}_3$ crystals, taken from [92, 93, 113].

Table 5

Compound	θ_N°, K	$\chi_{\perp}(0), \text{mole}^{-1}$	$\chi_z(0), \text{mole}^{-1}$	$M_s(0), \text{cgse mu/mole}$	$m_0, \%$	$\bar{H}_D = \frac{M_s(0)}{\chi_{\perp}(0)}, \text{kOe}$
MnCO_3	32.4	$43 \cdot 10^{-3}$	$45 \cdot 10^{-3}$	200	0.7	4.5
CoCO_3	18.1	$53 \cdot 10^{-3}$	$35 \cdot 10^{-3}$	1400	13	26
$\alpha\text{-Fe}_2\text{O}_3$	950	$32 \cdot 10^{-4}$	$35 \cdot 10^{-4}$	64	0.1	20

The above table gives the values of χ and M_s , extrapolated to 0°K; for $\alpha\text{-Fe}_2\text{O}_3$, these values are extrapolated from $T > 250^\circ\text{K}$, where ferromagnetism is known to exist. The quantity m_0 represents the weak ferromagnetic moment, as percentages of the maximum

possible moment for a given compound; this maximum moment is calculated on the assumption that the magnetic moments of all ions are completely parallel, taking for each ion the theoretical value of the magnetic moment in the free-ion state.

Table 5 indicates that the magnetic susceptibility of α -Fe₂O₃ and MnCO₃ is almost isotropic, but that of CoCO₃ is strongly anisotropic (χ_{\perp} is approximately 1.5 times greater than χ_{\parallel}). This difference between the susceptibilities is retained in the paramagnetic region above the Néel point: the paramagnetic susceptibility of α -Fe₂O₃ and MnCO₃ is isotropic, and that of CoCO₃ is 30% anisotropic at $T = 300^{\circ}\text{K}$. This means that α -Fe₂O₃ and MnCO₃ have isotropic g factors, which is in good agreement with the fact that the Fe³⁺ and Mn²⁺ ions are in the S state. The strong anisotropy of the magnetic properties of CoCO₃, both at low and high temperatures, indicates the considerable importance of the orbital magnetism and, consequently, possible g -factor anisotropy. This is again in agreement with the fact that the ground state of the free Co²⁺ ions is the F state [93]. It is characteristic also that m_0 of CoCO₃ is an order of magnitude greater than m_0 of MnCO₃. The value $m_1 = 13\%$ of CoCO₃ represents the "deviation" of the magnetic moments of the sublattices from the antiferromagnetic axis by about 7° .

To solve the problem of the nature of weak ferromagnetism in these crystals, it is necessary to study experimentally their resonance properties. Such studies would not only give, by an independent method, the parameters H_{EA} , \overline{H}_D , etc., but also the separate components of the g tensor (see also Chap. IX).

CHAPTER VII

Weak Ferromagnetism in Uniaxial Crystals of Odd Antiferromagnetic Structure with Respect to the Principal Axis

We have already mentioned that the characteristic property of antiferromagnetic structures of the n^+2^- type, even with respect to the principal axis, is the isotropy (in the first approximation) of their magnetic properties in the basal plane. The weak ferromagnetic moment of these structures is always perpendicular to the antiferromagnetic axis and may be described by a single parameter $\vec{d} = d + \tau A$. This property is due to the fact that the weak ferromagnetism invariant in the spin Hamiltonian $l_x m_y - l_y m_x \equiv [lm]_z$ is, for a given angle between vectors l and m , isotropic with respect to rotation about the Z axis, and its absolute value is a maximum when $m \perp l$.

The situation is different in uniaxial crystals with antiferromagnetic structures which are odd with respect to the principal axis. For these structures, the invariants responsible for weak ferromagnetism depend not only on the angle between l and m , but also on the orientation of l in the basal plane for a fixed value of this angle. It is therefore natural to expect that in structures which are odd with respect to the principal axis, weak ferromagnetism will be somewhat different from that in structures of the n^+2^- type.

In particular, the relationship (5.16) indicates that, for example, in the case of structures of the $4_z 2_d^+$ type, weak ferromagnetism is, in general, neither transverse nor longitudinal. The projection of the magnetic moment M along the direction of the vector l varies with rotation of the latter in the basal plane in accordance with the law

$$M_l = M_0 g_{xy} \sin 2\varphi.$$

There are several other special properties of weak ferromagnets with structures which are odd with respect to the principal symmetry axis. This chapter deals with such structures.

1. TETRAGONAL CRYSTALS. INVESTIGATION OF THEIR GROUND STATE AND MAGNETIZATION CURVES

According to Table 3, structures which are odd with respect to the principal axis may exist in tetragonal and hexagonal crystals. We shall consider first structures of the $4_z^-2_d^+$ and $4_z^-2_d^-$ types in tetragonal crystals. The former structure is exhibited by transition-metal fluorides FeF_2 , NiF_2 , CoF_2 , etc.

The form of all the invariants in the magnetic Hamiltonian (both those representing the anisotropy and those responsible for weak ferromagnetism) and the form of the g tensors is identical for both types of structure $4_z^-2_d^+$ and $4_z^-2_d^-$ if the coordinates X and Y of one of the structures are rotated through an angle of 45° about the Z axis, with respect to the axes used for the second of these two structures.* In other words, if the axes X and Y of structures of the $4_z^-2_d^-$ type are directed not along the sides of the basal square but along its diagonals, the invariants and the g tensors become the same as those for structures of the $4_z^-2_d^+$ type. It all reduces to the fact that we should direct the same coordinate axes of these two types of structure along symmetry axes (or planes) of the same parity. The descriptions of all the properties of weakly ferromagnetic crystals will then be exactly the same for the two types of structure.

We shall use the form of the magnetic Hamiltonian and the g tensors given in Tables 3 and 4 for structures of the $4_z^-2_d^+$ type.

In the case of the transition-metal fluorides just mentioned (which have this structure) this means that the axes X and Y should be directed as shown in Fig. 8.

The total magnetic-energy density, with allowance for an external field, may be represented in the form

$$\begin{aligned} \mathcal{H}(\mathbf{r}) = & \frac{A}{2} m^2 + \frac{a}{2} m_z^2 + \frac{b}{2} l_z^2 - d(l_x m_y + l_y m_x) + \\ & + \frac{1}{2} f l_x^2 l_y^2 - h_x(m_x + \tau l_y) - h_y(m_y + \tau l_x) - h_z m_z + \mathcal{H}_{\text{inhom}}, \end{aligned} \quad (7.1)$$

where the notation is the same as in the expression (6.1). The

*The data for tetragonal crystals are presented in Tables 3 and 4 in general coordinates, used in the International Crystallographical Tables.

above equation allows for the fact that the magnetic moment M of structures of the $4_z 2_d^+$ type is related to the vectors m and l by the expressions (5.16).

The minimization of \mathcal{H}_0 when $H = 0$ yields the following three types of solution:

$$\text{I. } \sin \theta = 0, \quad m = 0, \quad \text{if } b < 0; \quad (7.2)$$

$$\text{II}_1. \cos \theta = 0, \quad \sin 2\varphi = 0, \quad m = \pm \frac{d}{A}, \quad (7.3)$$

if

$$b > 0, \quad f + 4 \frac{d^2}{A} > 0; \quad (7.4)$$

$$\text{II}_2. \cos \theta = 0, \quad \cos 2\varphi = 0, \quad m = 0, \quad (7.5)$$

if

$$b > 0, \quad f - 4 \frac{d^2}{A} < 0. \quad (7.6)$$

State I, in which the vector l is directed along a tetragonal axis of a crystal, is again purely antiferromagnetic, since for this state the magnetization, according to (7.2) and (5.16), is $M_s = 0$.

In states II_1 and II_2 , the vector l lies in the basal plane and is directed either along one of the sides of the basal square (i.e., along the axes X or Y) or along one of the diagonals. Both these states are weakly ferromagnetic. In state II_1 , the spontaneous magnetic moment is, according to (5.16), perpendicular to the antiferromagnetic axis and its value is given by

$$M_s = M_0 g_{\perp} \left(\frac{d}{A} + \tau \right). \quad (7.7)$$

In state II_2 , the spontaneous magnetic moment is parallel to the antiferromagnetic axis, and its value is related only to the g -factor anisotropy:

$$M_s = M_0 g_{\perp} \tau. \quad (7.8)$$

We shall use the subscript "s" to denote not only M_s but also all other quantities (m , l , and φ) which represent the natural or spontaneous state (i.e., the equilibrium state for $h = 0$).

We shall now investigate the ground state of the system and the magnetization curves at $T = 0^\circ\text{K}$ as functions of the magnitude and direction of an external magnetic field. Once again, we can

use m_{\perp} , m_z and φ as independent variables for the weakly ferromagnetic states ($l \perp Z$). In terms of these variables, the ground-state energy is

$$\begin{aligned} \frac{\mathcal{H}_0}{V} = & \frac{A}{2} (m_{\perp}^2 + m_z^2) + \frac{a}{2} m_z^2 + dm_{\perp} l \cos 2\varphi + \\ & + \frac{f}{8} l^4 \sin^2 2\varphi - h_{\perp} m_{\perp} \sin (\varphi - \varphi_H) - h_{\perp} l \tau \sin (\varphi + \varphi_H) - \\ & - h_z m_z \quad (l = l_{\perp} = \sqrt{1 - m_{\perp}^2 - m_z^2}), \end{aligned} \quad (7.9)$$

where again φ_H is the azimuthal angle of the field H .

We have assumed that because m_{\perp} and $l_{\perp} = l$ are perpendicular, we can take

$$m_x = m_{\perp} \sin \varphi, \quad m_y = -m_{\perp} \cos \varphi. \quad (7.10)$$

In general, for arbitrary magnitudes and directions of the external field, the system whose energy is given by (7.9) is very complex, and the actual magnetization curves may depend very strongly on the relationship between the following three constants:

d , $A\tau$ and \sqrt{Af} , and on the value of h relative to these constants. Therefore, to determine the main features of weak ferromagnetism in structures of the $4_z^- 2_d^+$ type we shall consider the most typical special cases.

First, let us assume that the magnetic field is directed along a tetragonal axis, i.e., $h_x = h_y = 0$ and $h_z = h$. Therefore, as is easily seen from the condition for a minimum \mathcal{H}_0 , the transverse components of m and l and, consequently, also of M , retain their previous spontaneous values given by the relationships (7.3) and (7.7) or (7.5) and (7.8), respectively, for the states Π_1 and Π_2 . Moreover, we have also the components m_z and M_z :

$$m_z = \frac{h_z}{A - a}, \quad M_z = \chi_z H, \quad (7.11)$$

where χ_z is given by (6.10). Thus the magnetization curve along the principal axis of a crystal is again the same as for normal antiferromagnets.

Now let us assume that the magnetic field is perpendicular to the tetragonal axis so that $h_{\perp} = h$ and $m_{\perp} = m$. We shall consider first the magnetization curves for fields whose values cover a wide range

$$0 < h < A, \quad (7.12)$$

and whose directions either coincide with the direction of the

spontaneous magnetic moment M_s , or are perpendicular to this moment. We shall take separately the cases for which the spontaneous states are Π_1 and Π_2 .

A. State Π_1 ($Af + 4d^2 > 0$)

1. First let us deal with a magnetic field parallel to the direction of the spontaneous magnetic moment, i.e., $\varphi_H = 0$ or $\varphi_H = \frac{\pi}{2}$ (for $\varphi_s = \frac{\pi}{2}$ or $\varphi_s = 0$).

In this case, the directions of the vectors m and l remain the same as in the initial spontaneous state, and the values of m_H and M_H are*

$$m_H = \frac{d + h}{A}, \quad (7.12)$$

$$M_H = M_s + \chi_{\perp} H, \quad (7.13)$$

where M_s is in the form given by (7.7) or (6.3), and the magnetic susceptibility χ_{\perp} is given again by (6.4). Thus, in this case, the ground state and the magnetization curve are exactly the same as for structures of the n^+2^- type.

2. Now let us take a magnetic field parallel to the spontaneous direction of the vector l , i.e., $\varphi_H = \frac{\pi}{2}$ or $\varphi_H = 0$ (which corresponds to the initial angles $\varphi_s = \frac{\pi}{2}$ or 0).

a) $d \gg \tau A$, $d^2 \gg Af$.

In this case, both weak ferromagnetism and basal-plane anisotropy are mainly due to the term with the constant d in the magnetic-energy expression (7.9).

Let us assume that in the initial state $\varphi_s = \frac{\pi}{2}$, i.e., the vector l_s is parallel to the Y axis (and, consequently, the vector M_s is parallel to the X axis). Assuming that $\varphi_H = \frac{\pi}{2}$ and minimizing \mathcal{H}_0 , we find the following three solutions for φ and $m_H = m_y$ as a function of h :

$$1. \cos \varphi = -\frac{h}{4d}, \quad m_H = \frac{h}{4A} \left[1 + 2 \left(\frac{h}{4d} \right)^2 \right]; \quad (7.14)$$

*The expression (7.12) is obtained for $m^2 \ll 1$ from the more general equation (7.16), shown schematically in Fig. 15 (curve 3). [The numbering of equations follows the Russian text; (7.12) appears twice—here and on p. 121.—Ed.]

$$2. \cos \varphi = -1, \quad h = Am_H + d \frac{1 - 2m_H^2}{\sqrt{1 - m_H^2}}$$

$$\text{when } m^2 \ll 1, \quad m_H = \frac{h - d}{A}; \quad (7.15)$$

$$3. \cos \varphi = 1, \quad h = Am_H - d \frac{1 - 2m_H^2}{\sqrt{1 - m_H^2}}$$

$$\text{when } m^2 \ll 1, \quad m_H = \frac{h + d}{A}. \quad (7.16)$$

The solution 3 represents the absolute minimum of the energy. However, it is separated by an energy barrier from the initial state. Therefore, on increase of the field intensity, beginning with $h = 0$, the solution 1 is realized first since it represents the state which immediately follows the initial state. This solution describes the process of gradual rotation of the vectors m and l in the basal plane on increase of h , which ends when $h = 4d$. The solution 1 then transforms to solution 2.

Figure 15 (curve 2) shows that solution 2 represents the magnetization curve that would be obtained if, in the initial state,

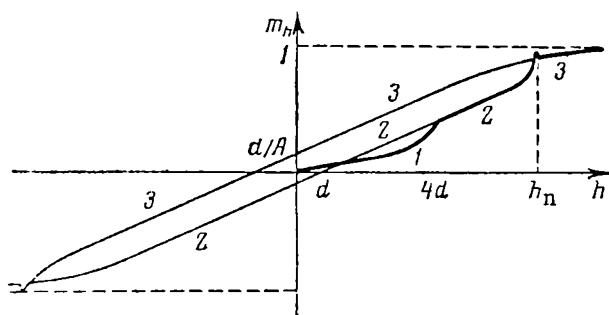


Fig. 15

the external field were applied opposite to the direction of the spontaneous magnetization M_s . Due to the presence of an energy barrier between solutions 2 and 3, the system "remembers" the state with a negative value of M_s even after the resultant magnetization in a field $H > H_D$ changes its sign [formula (5.15)].

Then, returning to $h = 0$, we reach a state with $m_s = -\frac{d}{A}$. We note that the difference between the magnetization curves for states 2 and 3 is due to the opposite directions of the vector l for these states. For a transition to occur from the metastable state 2 to the absolutely stable state 3, the vector l must reverse. This can happen only when the field is increased to a value

$h = h_n \approx A \left[1 - \frac{3}{2} \left(\frac{d}{A} \right)^{2/3} \right]$, above which the second derivative of \mathcal{H}_0 with respect to m_\perp for solution 2 becomes negative and, consequently, the solution itself becomes unstable.*

When $h = h_n$, the direction of l reverses and the system finally reaches the state equilibrium corresponding to the solution 3. Near the point $h = h_n$, an interesting singularity of the magnetization curve is observed: having reached its maximum value $m_H \simeq 1 - \frac{1}{2} \left(\frac{d}{A} \right)^{2/3}$ (when $\partial m_H / \partial h$ is infinite), the magnetization suddenly drops to the curve 3 and then again rises along this curve up to saturation. On reduction of the field from values $h > h_n$, demagnetization proceeds along curve 3.

The complete magnetization curve for this case ($H \parallel l_s$) is the heavy curve in Fig. 15, the initial portion of which (when $h \ll A$) may be represented, according to (7.14) and (7.15), in the form

$$\begin{aligned} M_H &= \frac{1}{4} \chi_\perp H \left[1 + \frac{1}{8} \left(\frac{H}{H_D} \right)^2 \right] \text{ when } H \leq 4H_D, \\ M_H &= \chi_\perp (H - H_D) \text{ when } H \geq 4H_D. \end{aligned} \quad (7.17)$$

Thus, the magnetic susceptibility in weak fields ($H \ll 4H_D$) is four times smaller than in strong fields $H > 4H_D$.

Figure 15 also shows the schematic hysteresis loop that would be obtained by the cyclic magnetization of a crystal along the direction of m_s in strong fields up to $h > h_n$.

Our conclusions about the form of the magnetization curves have obviously been influenced by the purely classical concepts of the magnetic sublattices, which permit us to speak of a definite direction of the vector l and of the reverse of this direction. In particular, one should regard with caution the conclusion that it is impossible to reverse the magnetization of a weak ferromagnet (i.e., to rotate the vector m_s from one spontaneous direction to another) except in very strong fields $H \sim H_E$. From the point of view of quantum mechanics, a definite fixed magnetic sublattice may exist, if at all [116], for only a finite interval of time. Therefore, such magnetization reversal may occur in weaker fields but only after some finite time interval comparable with the sublattice "lifetime." It is possible that such a reversal of the weak ferromagnetic moment (of piezomagnetic origin) accompanied by a reversal of the vector l , was observed by Borovik-Romanov [117] in CoF_2 crystals (the magnetization reversal in a field of $\sim 10^3$ oersteds, directed opposite to m_s , occurred in ~ 10 min).

*A more accurate value of h_n can be found by solving simultaneously (5.15) and $\frac{\partial^2 \mathcal{H}_0}{\partial m_\perp^2} = 0$.

In any case, experimental investigations of magnetization reversal processes in weak ferromagnets are of great interest in connection with the sublattice "lifetime," which would fix the limits of applicability of the classical concepts. Weak ferromagnets are of special importance because their thermodynamic potential contains mixed terms of the $m_z l_z$ type, which makes it possible to fix definite directions of the magnetic moments of the sublattices (including their signs). By causing a certain component of the vector m to appear under the action of an external field, we are inducing a definite component of the vector l with a definite sign.

b) $A\tau \gg d$, \sqrt{Af} .

In this case, weak ferromagnetism is mainly due to the g -factor anisotropy; the term with the constant d in \mathcal{H} affects only the critical-field value at which the vector l reverses. Minimizing \mathcal{H} for $\varphi_H = \frac{\pi}{2}$, we now find:

$$\begin{aligned} 1. \quad \cos \varphi (1 - 2 \cos^2 \varphi) &= \frac{A\tau}{Af - 4d^2} h, \quad m_H = \cos \varphi \frac{(d \cos 2\varphi + h \cos \varphi)}{A}; \\ 2. \quad \cos \varphi &= 1, \quad m_H = \frac{d + h}{A}. \end{aligned} \quad (7.18)$$

An investigation of the function $\cos \varphi(h)$, defined by (7.18), shows that this function has a maximum at

$$h = h^* = \sqrt{\frac{2}{27} \frac{Af + 4d^2}{A\tau}}. \quad (7.19)$$

In fields $h < h^*$, the function $\cos \varphi(h)$ increases monotonically with increase in h and then, having reached a maximum, $\cos \varphi(h^*) = \frac{1}{\sqrt{6}}$, decreases when $h > h^*$. This means that the continuity of the rotation of the vector l (corresponding to the solution 1) is disturbed at $h = h^*$ and the system shifts discontinuously into the state described by solution 2.

The variation of the magnetization with the field can then be represented approximately by

$$\begin{aligned} M_H &= M_s \cos \varphi \text{ when } H \leq H^*, \\ M_H &= M_s + \chi_{\perp} H \text{ when } H \geq H^*, \end{aligned}$$

where $\cos \varphi$ is the solution of (7.18), $M_s \simeq M_0 g_{\perp} \tau$ and

$$H^* = M_0 g_{\perp} h^*. \quad (7.20)$$

This dependence is shown graphically in Fig. 16 for $h \ll A$.

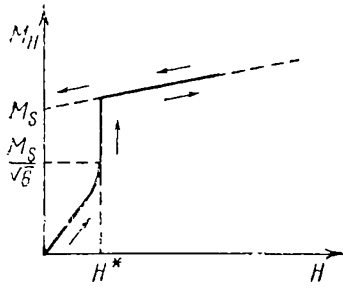


Fig. 16

The initial magnetic susceptibility for $H \ll H^*$ (when $\cos \varphi \ll 1$) may be given explicitly by:

$$M_H = \chi_{\perp} \frac{(A\tau)^2}{A\bar{f} + 4d^2} H = \chi_{\perp} \frac{A\tau}{h^*} H. \quad (7.21)$$

It is interesting that in the case "a" (see above) the initial susceptibility was less than χ_{\perp} but here it is considerably greater than the latter value (because $A\tau \gg h^*$).

In contrast to case a, the hysteresis is restricted to the region of relatively weak fields $|h| \leq h^*$ (Fig. 16).

In both the foregoing cases, we have assumed that the anisotropy constant \bar{f} is small. Otherwise, if this constant is so large that

$$\sqrt{A\bar{f}} \gg d, A\tau,$$

the magnetization curve is qualitatively similar to the curve shown in Fig. 16. Moreover, the magnetization in the initial part of the curve is again given by (7.21). However, the critical field in which the vector l is reversed is now given by the relationship

$$h_{cr} \approx \sqrt{A\bar{f}},$$

which is valid also for normal antiferromagnets without weak ferromagnetism.

B. State II_2 ($A\bar{f} + 4d_2 < 0$, $M_s \parallel l_s$)

For this state, a detailed analysis will be given for the most interesting case, when the following condition is satisfied

$$A\tau \gg \sqrt{A|\bar{f}|}. \quad (7.22)$$

1. Let us assume that the external magnetic field is parallel to the spontaneous magnetization in the initial state: $H \parallel M_s \parallel l_s$. Moreover, let us assume that $\varphi_H = \varphi_s = \frac{\pi}{4}$. The minimum solutions then have the form

1. $\cos\left(\varphi - \frac{\pi}{4}\right) = 1$, $m_h = 0$, when $h \leq A\tau$;
2. $\cos\left(\varphi - \frac{\pi}{4}\right) = \frac{A\tau}{h}$, $m_H = \frac{h}{A} \left[1 - \left(\frac{A\tau}{h}\right)^2\right]$, when $h \geq A\tau$.

The antiferromagnetic axis in fields up to $h = A\tau$ remains parallel to the external field, but on further increase in the external field intensity the vector \mathbf{l} begins to rotate, approaching asymptotically the direction perpendicular to \mathbf{H} in fields $h \gg A\tau$.

The corresponding formulas for the magnetization are of the following form:

$$M_H = M_s = M_0 g_{\perp} \tau \quad \text{when } H \leq \tau H_E = M_0 g_{\perp} A \tau; \quad (7.23)$$

$$M_H = \chi_{\perp} H \quad \text{when } H \geq \tau H_E. \quad (7.24)$$

This dependence of the magnetization on the field is shown graphically in Fig. 17a for $h \ll A$.

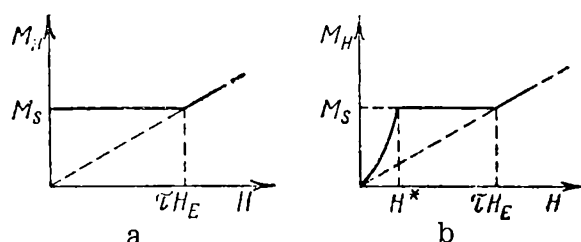


Fig. 17

It is interesting that the spontaneous magnetic moment appears here only in fields $H < \tau H_E$. On extrapolation to $H = 0$ from stronger fields, we obtain $M_s = 0$.

2. If the external magnetic field is perpendicular to the direction of M_s (and, consequently, to \mathbf{l}_s) the behavior of the system is described by the following three self-consistent solutions:

$$1. \cos\left(\varphi - \frac{\pi}{4}\right) \left[1 - 2 \cos^2\left(\varphi - \frac{\pi}{4}\right)\right] = \sqrt{\frac{2}{27}} \frac{h}{h^*} \text{ when } h \leq h^*; \quad (7.25)$$

$$2. \sin\left(\varphi - \frac{\pi}{4}\right) = 0 \text{ when } h^* \leq h \leq A\tau; \quad (7.26)$$

$$3. \cos\left(\varphi - \frac{\pi}{4}\right) = \frac{A\tau}{h} \text{ when } h \geq A\tau. \quad (7.27)$$

The value of m for the three solutions is obtained from

$$m = \frac{d \sin 2\left(\varphi - \frac{\pi}{4}\right) + h \sin\left(\varphi - \frac{\pi}{4}\right)}{A} \quad (7.28)$$

using the value of the angle φ given by (7.25), (7.26) or (7.27). The critical field H^* is again given by (7.19) and (7.20).

The first solution describes a gradual rotation of the vector l corresponding to a continuous increase in $\cos(\varphi - \pi/4)$. When $h = h^*$, this rotation ends by a jump into the state $l \parallel h$, corresponding to the solution 2. The rotation is described by an equation analogous to (7.18) for the case 2. However, it proceeds in the opposite direction since, in the case referred to, we dealt with a transition from $l \parallel h$ to $l \perp h$, and here we have the opposite transition, from $l \perp h$ to $l \parallel h$. It should be pointed out also that here $M_s \parallel l_s$, while in the case 2 $M_s \perp l_s$.

The second solution given by (7.26) is identical with state 1 for $H \parallel M_s \parallel l_s$ (discussed above) and therefore the subsequent behavior of the system when $h > h^*$ is exactly the same as before.

The initial portion of the magnetization curve up to $h = h^*$ coincides with the initial portion shown in Fig. 16, but at $h = h^*$ this curve should transform into that given in Fig. 17a. The complete magnetization curve is shown in Fig. 17b.

We shall deal next with the angular dependence of weak ferromagnetism in the basal plane, i.e., the dependence of M_H on the angle φ_H . For this purpose, we shall consider magnetic fields which are strong compared with the effective magnetic anisotropy field in the basal plane, i.e.,

$$h \gg \sqrt{|Af + 4d^2|}. \quad (7.29)$$

The field direction in the basal plane may be arbitrary. We shall take separately the cases in which weak ferromagnetism is mainly due to the noncollinearity of the angular momenta ($d \neq 0$, $\tau = 0$), or due only to the g -factor anisotropy ($d = 0$, $\tau \neq 0$).

a) $d \neq 0$, $\tau = 0$.

In this case, the relationship (7.29) is the condition for $M \parallel H$ (i.e., $M_H = M$). The vector l is then perpendicular to H so that when $\tau = 0$ the directions of m and M coincide and $l \perp M$. Thus, assuming that $\varphi = \varphi_H + \frac{\pi}{2}$, we find from the condition for minimum \mathcal{H}_0

$$m = \frac{d \cos 2\varphi - h}{A}. \quad (7.30)$$

Consequently,

$$M_H = M_s(\varphi_H) + \chi_{\perp} H, \quad (7.31)$$

where

$$M_s(\varphi_H) = M_s \cos 2\varphi_H, \quad M_s = \frac{M_0 g_{\perp} d}{A}. \quad (7.32)$$

The formula (7.32) gives the angular dependence of the spontaneous magnetic moment found by extrapolating to $H = 0$ from fields in which condition (7.29) is satisfied. This dependence is shown graphically in Fig. 18, which shows the strong anisotropy of weak ferromagnetism in the present case. On the other hand, the magnetic susceptibility in the basal plane is, in the first approximation, isotropic and equal to the transverse magnetic susceptibility of a normal ferromagnet.

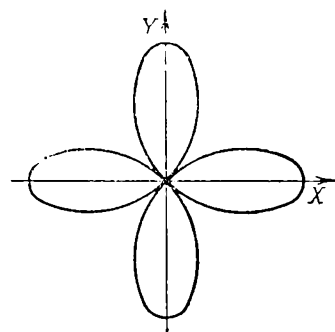


Fig. 18

b) $\tau \neq 0, d = 0$.

In this case, minimization of \mathcal{H}_0 gives the following system of equations for determining M_H as a function of h and φ_H :

$$M_H = M_0 g_{\perp} \left[\frac{h}{A} \sin^2 (\varphi - \varphi_H) + \tau \sin (\varphi + \varphi_H) \right], \quad (7.33)$$

$$A\tau \cos (\varphi + \varphi_H) = -h \sin (\varphi - \varphi_H) \cos (\varphi - \varphi_H). \quad (7.34)$$

For an arbitrary relationship between h and $A\tau$, the above equations lead to a very complex dependence $M_H(h, \varphi_H)$. Therefore, we shall consider two possible special limiting cases:

1) $h \ll A\tau$:

$$M_H = M_0 g_{\perp} \left(\tau + \frac{h}{A} \cos^2 2\varphi_H \right); \quad (7.35)$$

2) $h \gg A\tau$:

$$M_H = M_0 g_{\perp} \left(\tau \cos 2\varphi_H + \frac{h}{A} \right). \quad (7.36)$$

In the first case, the spontaneous magnetic moment obtained by extrapolation to $H = 0$ is isotropic and equal to its initial value $M_s = M_0 g_{\perp} \tau$. However, the magnetic susceptibility is anisotropic:

$$\chi(\varphi_H) = \chi_{\perp} \cos^2 2\varphi_H. \quad (7.37)$$

In the second case, similar to that with $d \neq 0$ and $\tau = 0$ (see above), the extrapolated value of the spontaneous magnetic moment is anisotropic but the magnetic susceptibility is isotropic, i.e.,

$$M_s(\varphi_H) = M_s \cos 2\varphi_H, \quad M_s = M_0 g_{\perp} \tau; \quad (7.38)$$

$$\chi(\varphi_H) = \chi_{\perp}. \quad (7.39)$$

Thus, our discussion of the magnetization curves at $T = 0^\circ\text{K}$ shows that, in contrast to the n^+2^- -type structures, the magnetic properties of weak ferromagnets of the $4_z^-2_d^+$ or $4_z^-2_d^-$ -type structures may be strongly anisotropic in the basal plane. Moreover, the two mechanisms of weak ferromagnetism lead, in general, to qualitatively different results and, therefore, to describe the properties of weak ferromagnets of the $4_z^-2_d^-$ type we must, in general, take into account the value of both d and τ .

2. TETRAGONAL CRYSTALS. SPIN WAVES AND TEMPERATURE DEPENDENCE OF THE WEAK FERROMAGNETIC MOMENT

We shall now consider the spin-wave spectrum and the temperature dependence of the weak ferromagnetic moment in states II_1 and II_2 . We shall deal only with the simplest cases when an external magnetic field is directed along the spontaneous magnetization M_s .

In state II_1 , the equilibrium vectors m and l are governed by the relationships [cf. (7.3) and (7.12)]

$$\cos \theta = \sin 2\varphi = 0, \quad l = l_\perp = \sqrt{1 - m^2}, \quad m = m_\perp = \frac{d + \tau h}{A}.$$

Considering small oscillations of m and l about their equilibrium positions, we can easily find from the complete Hamiltonian (7.1) the following expressions for the energy of the spin waves (again for $h \ll A$):

$$\varepsilon_{1k} = \frac{1}{I_0} [AB_k + Af + 4d^2 + h^2 + h(5d + \tau A)]^{1/2}, \quad (7.40)$$

$$\varepsilon_{2k} = \frac{1}{I_0} [AB_k + Ab + d^2 + h(d + \tau A)]^{1/2}.$$

Comparison of the above expressions with the corresponding expressions (6.12) for the n^+2^- -type structures shows basic differences between the former and the latter. First, in the present case, the energy of the weak ferromagnetism, i.e., the term with d in the Hamiltonian (7.1), gives rise to an energy gap in the first mode of the spin waves, even if $f = 0$ and $h = 0$. Second, again in the present case, this energy makes unequal contributions to the term linear in h in the first and second modes (the contribution to the first mode is five times as large as that to the second mode) while in the expressions (6.12) these contributions are equal. We shall see that these differences may affect the observed static and dynamic properties of the two types of weak ferromagnet.

Using the expressions (7.40) for the spin-wave energy we can calculate the temperature correction to the magnetization. The total magnetization is again of the form given by (7.13) but the magnetic susceptibility $\chi_{\perp}(T)$ is given by the expression (6.15) while the spontaneous magnetization is given by the following formulas:

$$(i) \quad \frac{V \overline{Af + 4d^2}}{I_0} \ll \kappa T \ll \frac{V \overline{Ab + d^2}}{I_0}, \quad (7.41)$$

$$M_s(T) = M_s(0) (1 - \eta_1 T^2), \quad \eta_1 = \left(\frac{1}{2} + \frac{2d}{d + \tau A} \right) \eta;$$

$$(ii) \quad \frac{V \overline{Ab + d^2}}{I_0} \ll \kappa T \ll \kappa \Theta_N, \quad (7.42)$$

$$M_s(T) = M_s(0) (1 - \eta_2 T^2), \quad \eta_2 = \left(1 + \frac{2d}{d + \tau A} \right) \eta.$$

To make the comparison more convenient, we have used the same coefficient η as in the formulas (6.14)-(6.16).

It is evident that the ratio of the coefficients η_1 and η_2 of T^2 in the formulas for the temperature dependence of $M_s(T)$ in the temperature ranges (i) and (ii) may depend on the relationship between d and τA . This ratio is identical with the corresponding ratio for the n^{+2} -type structures (which is always 1/2) only if $d \ll A\tau$. If the converse is true ($d \gg A\tau$), then in the present case the ratio of the coefficients η_1 and η_2 is equal to 5/6.

The formulas (7.41) and (7.42) exhibit another singularity of the temperature dependence of M_s : the spontaneous magnetization may rise with temperature at low temperatures because, depending on the relationship between d and τA , coefficients η_1 and η_2 may be either positive or negative. Assuming that the direction of the spontaneous magnetic moment is positive, we can assume that in all cases

$$d + \tau A > 0. \quad (7.43)$$

However, if also $d < 0$, then the coefficient of T^2 is always negative so that the condition

$$5d + A\tau < 0 \quad (7.44)$$

is satisfied by the formula (7.41), and the condition

$$3d + A\tau < 0 \quad (7.45)$$

is satisfied by the formula (7.42).

Thus, if the parameters τA and d have opposite signs and satisfy the inequality

$$3 < \left| \frac{A\tau}{d} \right| < 5, \quad (7.46)$$

then the spontaneous magnetization is a rising function of temperature in temperature range (i) and a falling function in temperature range (ii). If the condition

$$1 < \left| \frac{A\tau}{d} \right| < 3, \quad (7.47)$$

is obeyed, then $M_s(T)$ increases with increase of T in both temperature ranges.* In all other cases, the spontaneous magnetization, as in the case of weak ferromagnets of the n^+2^- type, always decreases on increase of temperature.

It is interesting to note that the rise of the magnetization with temperature was observed in the intermetallic compound $\text{Mn}_{3.4}\text{Ge}$. This compound has a tetragonal structure and very weak spontaneous magnetization of the order of $0.1 \mu_B$ per manganese atom (11 cgs emu/g). However, since very impure polycrystalline samples of $\text{Mn}_{3.4}\text{Ge}$ were used and the experimental data were few [118], we cannot yet conclude that this is due to anomalous temperature dependence of the weak ferromagnetic moment just discussed.

We shall now consider the energy spectrum and the temperature dependence of the magnetization for state II_2 . The general, very cumbersome expression for the spin-wave energy of this state (in fields $h < A\tau$) will not be given here.** We shall quote only the

*At sufficiently high temperatures, $M_s(T)$ passes through a maximum and then decreases on increase of temperature, even in this case (because the magnetization must disappear at the Néel point). However, this part of the temperature dependence of M_s is outside the limits of applicability of the spin-wave theory.

**It is given by (D.5) in the Appendix D, with the following values of the coefficients:

$$\begin{aligned} \alpha_1 &= \frac{1}{2I_0} \left[A + A_k + B_k + \frac{1}{2}(a+b) - 3d + h(1+\tau) \right]; \\ \alpha_2 &= \frac{1}{2I_0} \left[A + A_k + B_k + \frac{1}{2}(a+b) + 3d - h(1-\tau) \right]; \\ \alpha_3 &= -\frac{1}{4I_0}(a-b); \\ \beta_1 &= -\frac{1}{2I_0} \left[d + \frac{1}{2}(a+b) \right]; \\ \beta_2 &= \frac{1}{2I_0} \left[d - \frac{1}{2}(a-b) \right]; \\ \beta_3 &= \frac{1}{2I_0} \left[A + A_k - B_k + \frac{1}{2}(a-b) \right]. \end{aligned}$$

approximate expression obtained by neglecting all the magnetic anisotropy terms, assuming that $a = b = f = d = 0$. In this approximation, we have

$$\varepsilon_k^{(1,2)} = \frac{1}{I_0} \sqrt{(A \pm A_k \pm h\tau)(B_k \pm h\tau) \pm h}. \quad (7.48)$$

Using the conditions $A_k, h\tau \ll A$, this expression can be also written as follows:

$$\varepsilon_k^{(1,2)} = \sqrt{I_{\perp} k_{\perp}^2 \pm I_z k_z^2 \pm \mu_{\perp}^2 (\tau H_E) H \pm \mu_{\perp} H}. \quad (7.49)$$

Using the above expression to calculate the temperature-dependent part of the magnetization, we easily find that the total magnetization is

$$M_H(T) = M_s(T) + \chi_{\parallel}(T) H, \quad (7.50)$$

where

$$M_s(T) = M_0 g_{\perp} \tau (1 - \eta T^2); \quad (7.51)$$

$$\chi_{\parallel}(T) = 4 \frac{M_0 g_{\perp}}{H_E} \eta T^2. \quad (7.52)$$

We note that χ_{\parallel} is identical with the parallel magnetic susceptibility of a normal antiferromagnet [cf., for example, (4.60) in Chap. IV].*

In this case the spontaneous magnetization decreases with increasing temperature but the magnetic susceptibility rises. Therefore, the temperature-dependent part of the magnetization

$$\Delta M_H(T) = - \frac{M_0 g_{\perp} \eta T^2}{H_E} (\tau H_E - 4H)$$

should change its sign at $H = \tau H_E/4$.

We can show that the above temperature dependence of the spontaneous magnetization of state II₂ remains valid even when the magnetic anisotropy terms are allowed for, provided we restrict ourselves to temperature range (ii).

*The magnetic susceptibility is identical in the state II₁ with χ_{\perp} , and in the state II₂ with χ_{\parallel} , because the magnetic field in both cases is parallel to the spontaneous magnetic moment, and this moment is in the former case at right angles and in the latter case parallel to the antiferromagnetic vector l . In general, the magnetic susceptibility, even at $T = 0^\circ\text{K}$, depends in a very complex way not only on the magnetic field direction but also on its intensity.

3. HEXAGONAL CRYSTALS. HIGHER-ORDER WEAK FERROMAGNETISM

Weak ferromagnetism associated with the second-order invariants in the magnetic Hamiltonian and with g -factor anisotropy cannot exist in antiferromagnets with structures of the $6_z^- 2_d^+$ type (here $2_d \equiv 2_x$ or 2_y). However, terms of higher (fourth) order (Nos. 13 and 14 in Table 3) may give rise to a spontaneous magnetic moment. Although weak ferromagnetism has not yet been detected in such antiferromagnets, we shall briefly consider their properties because they have certain special features characteristic only of this type of structure.

The invariants responsible for the weak ferromagnetism in $6_z^- 2_x^+$ and $6_z^- 2_y^+$ structures are interchanged by the substitution $x \rightleftharpoons y$, and therefore it is sufficient to consider only one case, for example, the $6_z^- 2_x^+$ -type structure exhibited by some antiferromagnetic crystals of the nickel-arsenide type. The energy density, including the sixth-order magnetic anisotropy terms, is given by

$$\begin{aligned} \mathcal{H}(\mathbf{r}) = & \frac{A}{2} m^2 + \frac{a}{2} m_z^2 + \frac{b}{2} l_z^2 + \frac{t}{2i} [(l_x + il_y)^3 - (l_x - il_y)^3] m_z + \\ & + r l_z [m_y (l_x^2 - l_y^2) + 2m_x l_x l_y] + e [(l_x + il_y)^6 + (l_x - il_y)^6] - \\ & - mh + H_{\text{inhom}}. \end{aligned} \quad (7.53)$$

Here, we have neglected the unimportant—for the present case, that is—difference between the g_\perp and g_{zz} factors (cf. group VII in Table 4).

The ground-state energy for $h \ll A$, $m^2 \ll 1$ is:

$$\begin{aligned} \frac{\mathcal{H}_0}{V} = & \frac{A}{2} m^2 + \frac{a}{2} m_z^2 + \frac{b}{2} (1 - m^2) \cos^2 \theta - r m_\perp \sin^2 \theta \times \\ & \times \cos \theta \cos 3\varphi + t m_z \sin^3 \theta \sin 3\varphi + e \sin^6 \theta \cos 6\varphi - m_\perp h_\perp - m_z h_z. \end{aligned} \quad (7.54)$$

Minimizing this expression when $h = 0$, we find three possible spontaneous states:*

- I. $\sin \theta = 0$, $m_\perp = m_z = 0$;
- II₁. $\cos \theta = 0$, $\sin 3\varphi = 0$, $m_\perp = m_z = 0$;
- II₂. $\cos \theta = 0$, $\cos 3\varphi = 0$, $m_\perp = 0$, $m_z = \pm \frac{t}{A+a}$.

The first two states are antiferromagnetic, and the third is weakly

*In general, a large number of solutions is obtained but if conditions $r \ll a$ and $m \ll 1$ are applied, only the three solutions listed above are found to be of interest.

ferromagnetic. The weakly ferromagnetic state is obtained when

$$\begin{aligned} b(A+a) + t^2 + 2e(A+a) &> 0, \\ t^2 + 4e(A+a) &> 0. \end{aligned} \quad (7.55)$$

In this case, in contrast to all the cases considered above, the spontaneous magnetic moment lies not in the basal plane but is directed along the hexagonal axis of the crystal.

We shall now consider the magnetization curves for the case when the spontaneous state is Π_1 or Π_2 .

It is easily shown that, irrespective of which of these two states is taken as the initial state, in fields

$$h_{\perp}^2 \gg t^2 + 4eA \text{ and } t^2, \quad (7.56)$$

the vector l remains in the basal plane and is perpendicular to h_{\perp} and, consequently, $m_{\perp} \parallel h_{\perp}$ for any direction of h . For both states

$$m_{\perp} = \frac{h_{\perp}}{A}, \quad (7.57)$$

$$m_z = \frac{t \cos 3\varphi_H + h_z}{A+a}. \quad (7.58)$$

Now let us assume that $h = 0$ and $h_z = h$. In this case, the magnetization curves for the initial states Π_1 and Π_2 will be different. For the state Π_2 , $\cos \theta = 0$, $\cos 3\varphi = 0$, $m_{\perp} = 0$ and

$$m_H = m_z = \frac{t+h}{A+a}. \quad (7.59)$$

If the state Π_1 is taken as the initial one, then the field transforms it into Π_2 by gradual rotation of the vector l in the basal plane, in accordance with the relationship

$$\sin 3\varphi = \frac{ht}{t^2 + 4e(A+a)}.$$

When $h = \bar{h} = \frac{|t^2 + 4e(A+a)|}{t}$ this rotation ends, and from then on the system behaves as in the state Π_2 . The magnetization curve for $h \leq \bar{h}$ is given by

$$m_H = \frac{h}{A+a} \left(1 + \frac{t}{\bar{h}} \right), \quad (7.60)$$

and when $h \geq \bar{h}$ it is given by (7.59). The magnetization curves for the two cases are shown in Fig. 19.

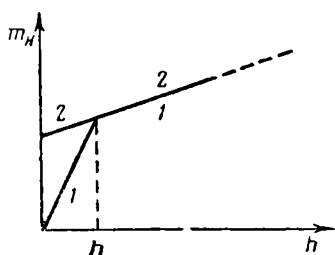


Fig. 19

We shall now give the approximate expressions for the spin-wave energy of the Π_2 state when $h \parallel m_s$ (i.e., for $h = h_z$), which are also applicable to the case when the initial state is Π_1 , if $h > \bar{h}$:

$$\varepsilon_{1k} = \frac{1}{I_0} [AB_k + 9(t^2 + 4eA + ht)]^{1/2},$$

$$\varepsilon_{2k} = \frac{1}{I_0} [AB_k + Ab + 4t^2 + 6eA + 5ht + h^2]^{1/2}.$$

Using these expressions, we shall calculate the temperature dependence of the spontaneous magnetization and of the magnetic susceptibility. The total magnetization is again given by a two-term formula*

$$M_H = M_s(T) + \chi_z(T) H, \quad (7.62)$$

in which

$$M_s(T) = M_0 g \frac{t}{A} \left(1 - \frac{9}{2} \eta T^2 \right) \text{ when } \kappa T \ll \frac{V \bar{A} b}{I_0}, \quad (7.63)$$

$$M_s(T) = M_0 g \frac{t}{A} (1 - 7\eta T^2) \text{ when } \kappa T \gg \frac{V \bar{A} b}{I_0}, \quad (7.64)$$

and $\chi_z(T)$ is the usual transverse magnetic susceptibility of an antiferromagnet along the Z axis whose temperature dependence is given by (6.16) or (6.17).

As mentioned previously, weak ferromagnetism has not yet been observed in antiferromagnets with the $6_z^- 2_d^+$ structure. This may be due to one of two causes: either the spontaneous magnetization of these antiferromagnets (whose antiferromagnetic axis lies in the basal plane) is too weak, or the overall weak ferromagnetic moment is zero because of the presence of domain structure. The point is that in the basal plane of a hexagonal crystal there are six equivalent directions along which the antiferromagnetic axis may lie. According to solution Π_2 , the weakly ferromagnetic moment m_s is parallel to the Z axis for three directions of the vector l_s , and antiparallel to the Z axis for the other three directions of l_s . Since antiferromagnetic domains of both these types are equally likely to form, the total moment of the sample becomes zero. To find whether weak ferromagnetism exists, it is necessary to apply a sufficiently strong field along the Z axis to establish

*[Again, the numbering of equations follows the Russian text; (7.61) has been omitted.—Ed.]

a single-domain structure.* The formation of domains of one type (with the same direction of the weak ferromagnetism moment) will also occur when a sample is cooled from the paramagnetic temperature region to the weakly ferromagnetic region in an external magnetic field.

It would be interesting to carry out these studies of single-crystal samples of antiferromagnetic crystals with the nickel-arsenide structure, in which the antiferromagnetic axis is perpendicular to the hexagonal axis.

*The magnitude of this field is unknown because there is as yet no theory of antiferromagnetic domain structure.

CHAPTER VIII

Weak Ferromagnetism in Orthorhombic Crystals

Weak ferromagnetism may also exist in crystals of lower symmetry (monoclinic and orthorhombic) but we shall consider only the latter. We shall use the basic property common to both monoclinic and orthorhombic crystals: the spontaneous antiferromagnetic axis of these crystals is completely determined by the magnetic anisotropy terms quadratic in l .

1. GROUND STATE AND MAGNETIZATION CURVES

If the Z axis is directed parallel to a symmetry axis (perpendicular to a symmetry plane) with respect to which an antiferromagnetic structure is even, the magnetic energy density of an orthorhombic weak ferromagnet is, in general, given by

$$\begin{aligned} \mathcal{H}(\mathbf{r}) = & \frac{1}{2} A m^2 + \frac{1}{2} a_1 m_x^2 + \frac{1}{2} a_2 m_y^2 + \frac{1}{2} b_1 l_x^2 + \frac{1}{2} b_2 l_y^2 + \\ & + d_2 m_y l_x - d_1 m_x l_y - h_x (m_x + \tau_1 l_y) - \\ & - h_y (m_y + \tau_2 l_x) - h_z m_z + \mathcal{H}_{\text{inhom}}. \end{aligned} \quad (8.1)$$

Here, in addition to the existing notation, we have introduced the following quantities: d_1 and d_2 are the parameters responsible for the noncollinearity of the angular momenta of the sublattices (the minus sign in front of one of them was selected on the grounds of convenience in later calculations); $\tau_1 = g_{xy}/g_{xx}$, $\tau_2 = g_{yx}/g_{yy}$.

Minimizing expression (8.1) with respect to the independent variables* when $\mathcal{H}_{\text{inhom}} = 0$ and $H = 0$, we find that there are now three possible states:

I. $\sin \theta = 0, m = 0.$

II. $\cos \theta = 0, \cos \varphi = 0, m_y = m_z = 0, m_x = m_{sx} = \pm \frac{d_1}{A + a_1 - b_2},$
 $M_x = M_{sx} \simeq \pm \frac{d_1 + \tau_1 A}{A} M_0 g_{xx}. \quad (8.2)$

III. $\cos \theta = 0, \sin \varphi = 0, m_x = m_z = 0, m_y = m_{sy} = \pm \frac{d_2}{A + a_2 - b_1},$
 $M_y = M_{sy} \simeq \pm \frac{d_2 + \tau_2 A}{A} M_0 g_{yy}. \quad (8.3)$

State I ($l \parallel Z$) is antiferromagnetic, but states II and III ($l \perp Z$) are weakly ferromagnetic. Which of these states is obtained depends on which of the corresponding energies

$$E_I = 0, E_{II} = \frac{b_2}{2} - \frac{d_1^2}{2(A + a_1 - b_2)} \quad \text{or} \quad E_{III} = \frac{b_1}{2} - \frac{d_2^2}{2(A + a_2 - b_1)}$$

has the least value.

We shall assume that the initial state is weakly ferromagnetic (for example, II) and we shall consider the normal magnetization curves (along the X, Y , and Z axes). We note that the conditions for this state are approximately (for $d_j \ll A$):

$$b_2 < 0, b_2 - b_1 < 0. \quad (8.4)$$

Let us assume first that $\tau_1 = \tau_2 = 0$ so that weak ferromagnetism is solely due to the noncollinearity of the angular momentum and consequently $M_H \parallel m_H$ always.

a) Magnetization along the direction of M_s , $h = h_x$.

In this case, the resultant vector m_H (like M_H) is directed along the field H and is related to it by

$$h = (A + a_1 - b_2) m_H - \frac{d_1 (1 - 2m_H^2)}{\sqrt{1 - m_H^2}}. \quad (8.5)$$

When $m_H^2 \ll 1$ (which occurs when $h \ll A$), instead of (8.5) we have, approximately,

$$m_H = \frac{d_1 + h}{A + a_1 - b_2}, \quad M_H = M_0 g_{xx} m_H. \quad (8.6)$$

*The independent variables are the modulus of the vector m , the polar (θ) and azimuthal (φ) angles of the vector l , and the angle γ , which gives the direction of the vector m in a plane perpendicular to l (cf. Chap. VI, Sec. 1).

The complete magnetization curve is shown schematically in Fig. 20a. Saturation is practically reached in fields $h_E \sim A$.

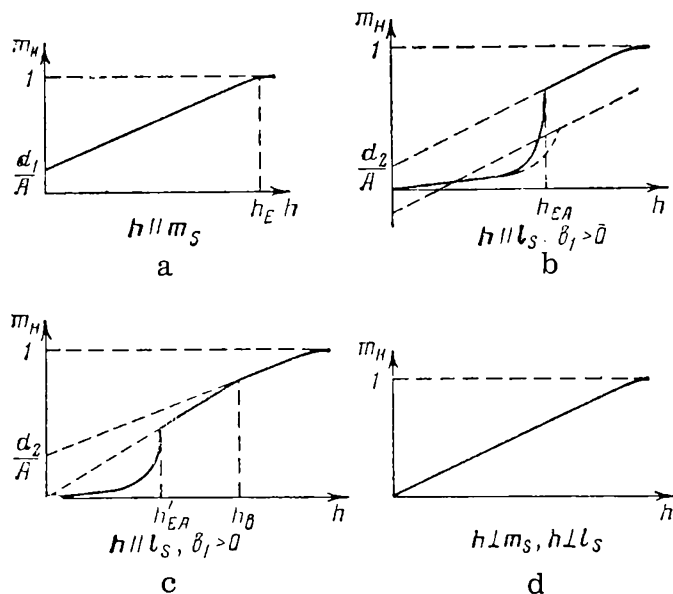


Fig. 20

b) Magnetization along the direction of l_s , $h = h_y$.

Here, the magnetic susceptibility of normal antiferromagnets without weak ferromagnetism (Chap. IV, Sec. 5) is zero up to a threshold field h_t , at which value the antiferromagnetic axis jumps suddenly to a position at right angles to the field. Roughly, the same picture exists here: the magnetization along the Y axis is very weak up to fields $h \sim h_t$, the magnitude of which is given approximately by $h_{EA} = \sqrt{A(b_1 - b_2)}$ for $b_1 < 0$ or $h'_{EA} = \sqrt{A|b_2|}$ for $b_1 > 0$. If $h \ll h_t$, then in both cases

$$m_H = \chi_{\parallel}(0) h, \quad (8.7)$$

where

$$\chi_{\parallel}(0) = \frac{d_1^2}{A^2(b_1 - b_2)}. \quad (8.8)$$

This longitudinal susceptibility due to weak ferromagnetism should only be a small fraction of the transverse susceptibility of an antiferromagnet,* because

$$\frac{\chi_{\parallel}(0)}{\chi_{\perp}(0)} \simeq \frac{d_1^2}{A(b_1 - b_2)}.$$

*The coefficient of proportionality between m_H and h will be denoted by the same symbol χ as the coefficient relating M_H to H , bearing in mind that in fact these two coefficients differ by a factor $(g_{\alpha\alpha} M_0)^2$.

If $b_1 < 0$, then in fields $h \sim h_{EA}$ the vector l rotates rapidly to a position parallel to the X axis, and m rotates to a position parallel to the field. When $h > h_{EA}$, the magnetization curve is given by an equation similar to (8.5), in which the following substitutions are made: $a_1 \rightarrow a_2$, $b_2 \rightarrow b_1$, and $d_1 \rightarrow d_2$. Approximately (if $h \ll A$)

$$m_H = \frac{d_2 \perp h}{A \div a_2 - b_1}. \quad (8.9)$$

We shall not give the complicated relationship for the dependence of m_H on h for fields close to h_{EA} . This dependence is qualitatively evident from the complete magnetization curve for this case (shown in Fig. 20b).

If $b_1 > 0$, then after transition to a state with $l \perp h$ and $m \parallel h$ in fields $h > h_{EA}$, the vector l in the XZ plane rotates gradually, with increase in fields, from a direction close to the Z axis to the direction of the X axis, so that

$$\sin \theta = \frac{d_2 m_H}{b_1 \sqrt{1 - m_H^2}} (\sin \varphi = 0). \quad (8.10)$$

Then

$$m_H = \frac{h}{A \div a_2 - d_2^2/b_1}. \quad (8.11)$$

The rotation of the vector l ends ($|\sin \theta| = 1$) when the field h reaches the value

$$h_b = \frac{A \div a_2 - d_2^2/b_1}{\sqrt{1 \div d_2^2/b_1^2}}, \quad (8.12)$$

i.e., earlier than saturation. When $h = h_b$ the straight line representing formula (8.11) transforms into a magnetization curve described by an equation of the (8.5) type in which the replacements $a_1 \rightarrow a_2$, $b_2 \rightarrow b_1$, and $d_1 \rightarrow d_2$ are made. The complete magnetization curve for this case is shown qualitatively in Fig. 20c.

The magnetization curves of Fig. 20b (the continuous curve) and 20c have been obtained on the assumption that the signs of d_1 and d_2 are the same. If the signs of d_1 and d_2 are different, then (8.5)—incorporating the substitutions just referred to—describes a magnetization reversal curve for which the initial state is that of spontaneous magnetization directed opposite to the field (compare

with curve 2 in Fig. 15 for structures of the $4_z^- 2_d^+$ type). Part of the magnetization curve for this case (for $b_1 < 0$) is shown dashed in Fig. 20b.

c) Magnetization along a direction perpendicular to l_s and M_s ; $h = h_z$. For this direction, the magnetization curve does not differ at all from the corresponding curve of a normal antiferromagnet, i.e., $m_H = \chi_\perp h$ for $h \leq h_E$ and $m_H = 1$ for $h \geq h_E$ (Fig. 20d).

The magnetization curves of Fig. 20 show the characteristic property of orthorhombic weak ferromagnets; i.e., the strong anisotropy of their magnetic properties. In fact, weak ferromagnetism appears only along one (the easiest) direction, while along the other two axes an orthorhombic crystal behaves in many respects like a normal antiferromagnet. If the second weakly ferromagnetic state III is the next one in order of energy ($E_{II} < E_{III} < E_I$), then in very strong fields of the order of $h_{EA} = \sqrt{A(b_1 - b_2)}$ the spontaneous magnetic moment may be rotated from its initial direction (X) to another possible direction (Y).^{*} Then, in accordance with (8.9), the value of m_H , extrapolated to $h = 0$, should differ from the value of m_s of (8.2), both in the initial state II and in the general state $d_2 \neq d_1$. Finally, if state I has lower energy than the state III ($E_{II} < E_I < E_{III}$), then extrapolating from the condition when the external field is applied, we find zero "spontaneous magnetization" along the direction of the vector l_s (this will apply until the magnetizing field reaches a value $h > h_b$, which is of the same order as the exchange fields, cf. Fig. 20c).

Allowance for g -tensor anisotropy for an arbitrary direction of the field may considerably affect the form of the magnetization curves. In general, when vector l is not directed (by an external field) along any of the orthorhombic axes (which are, as in tetragonal crystals, odd with respect to the fourfold axis) the weakly ferromagnetic moment is neither transverse nor longitudinal. However, for the magnetization curves along the principal directions discussed above, allowance for the tensor nature of the g factor is important only in the range of fields which rotate the vector l from one axis to another. On magnetization along M_s , the direction of the vector l is not affected and the quantity m_H (for $h \ll A$) is again given by formula (8.6). However, the magnetization is now

$$M_H \simeq \frac{d_1 + A\tau_1 + h}{A} M_0 g_{xx}, \quad (8.13)$$

^{*}More exactly, a transition from state II to state III occurs under the action of an external field. The resultant spontaneous moment, extrapolated to $H = 0$, may be positive or negative, depending on the relationship between the signs of d_1 and d_2 .

i.e., it differs from the corresponding expression in (8.6) by the substitution.

$$d_1 \rightarrow \bar{d}_1 = d_1 + A\tau_1. \quad (8.14)$$

On magnetization along l_s , the presence of $\tau_j \neq 0$, as in the case of odd tetragonal structures may strongly affect not only the value of the threshold field h_t but also the nature of the behavior of the system when the field is varied (particularly when $h \gtrsim h_t$). We shall not deal with this problem. Finally, in the case of magnetization at right angles to M_s and l , allowance for the g -factor anisotropy introduces no essential changes in the magnetization curve shown in Fig. 20d.

2. SINGULARITIES OF THE TEMPERATURE DEPENDENCE OF THE WEAK FERROMAGNETIC MOMENT

To deal with the temperature dependence of the spontaneous weak ferromagnetic moment, we shall quote the results of a calculation of the spin-wave spectrum for magnetization along the direction M_s . Allowing for the g -factor anisotropy when $h = h_x$ we find, from the general expression (8.1),

$$\begin{aligned} \varepsilon_{1k} &= \frac{1}{I_0} \{A(b_1 - b_2) + 2d_1(d_1 - d_2) + \\ &\quad + h[2(d_1 - d_2) + \bar{d}_1] + h^2 + AB_k\}^{1/2}, \\ \varepsilon_{2k} &= \frac{1}{I_0} \{A|b_2| + d_1^2 + h\bar{d}_1 + AB_k\}^{1/2}. \end{aligned} \quad (8.15)$$

As in the case of normal orthorhombic antiferromagnets (Chap. IV, Sec. 5), both spin-wave spectrum modes have gaps determined by the geometric mean values of the exchange and second-order magnetocrystalline energies.

Using the relationship (4.56), it is easy to obtain a general formula which gives the temperature dependence $M_s(T)$:

$$\begin{aligned} M_s(0) - M_s(T) &= \mu_x \sum_k \frac{\bar{d}_1 + 2(d_1 - d_2)}{2\varepsilon_{1k} \left[\exp\left(\frac{\varepsilon_{1k}}{\kappa T}\right) - 1 \right]} + \\ &+ \mu_x \sum_k \frac{\bar{d}_1}{2\varepsilon_{2k} \left[\exp\left(\frac{\varepsilon_{2k}}{\kappa T}\right) - 1 \right]}, \quad (\mu_x = \mu_B g_{xx}). \end{aligned} \quad (8.16)$$

Depending on the relationship between the parameters d_1 , $d_1 - d_2$, ε_{10} , and ε_{20} , the first and second sums in the right-hand part of (8.16) may have the same or opposite signs. Consequently, the

whole right-hand part of (8.16) may be positive or negative at different temperatures. This leads to the possibility of various singularities in the temperature dependence of M_s of orthorhombic crystals. We shall now consider the most typical of these singularities.

$$1) \quad \kappa T \gg \varepsilon_{10}, \varepsilon_{20}; \quad (8.17)$$

$$M_s(0) - M_s(T) = M_s(0) \left(1 + \frac{d_1 - d_2}{\bar{d}_1} \right) \eta T^2.$$

In this case, the weak ferromagnetic moment decreases with increase of temperature provided the following inequality does not hold:

$$\bar{d}_1 + d_1 - d_2 < 0. \quad (8.18)$$

When this inequality is obeyed, the spontaneous magnetization should increase with temperature in the same way as for tetragonal crystals (Chap. VII, Sec. 2). Both these possibilities are shown schematically in Fig. 21a.

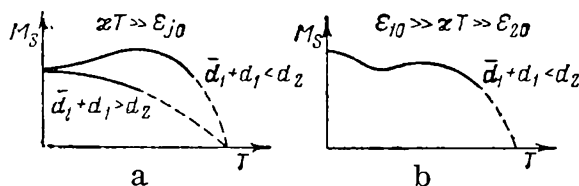


Fig. 21

$$2) \quad \varepsilon_{10} \gg \varepsilon_{20}, \varepsilon_{10} \gg \kappa T.$$

In this case, M_s is always a falling function of temperature. In particular, with the additional condition $\kappa T \gg \varepsilon_{20}$, we have

$$M_s(0) - M_s(T) = M_s(0) \frac{1}{2} \eta T^2. \quad (8.19)$$

Considering these two cases together, it is evident that not only the value of the coefficient of T^2 but also its sign may change from one case to the other if the inequality (8.18) holds. Then, $M_s(T)$ will first decrease with increase of temperature for $\kappa T \ll \varepsilon_{10}$ and then increase for $\kappa T \gg \varepsilon_{10}$. Consequently, we may have the complex nonmonotonic temperature dependence $M_s(T)$ shown in Fig. 21b. This possibility does not exist for crystals of higher symmetry.

The energy gaps ε_{j0} for spin waves in orthorhombic crystals (provided the anisotropy constants b_2 and $b_1 - b_2$) are sufficiently large) may be so great that the condition $\varepsilon_{j0} \ll \kappa T \ll \kappa \Theta_N$ cannot be satisfied by any of the spin-wave modes. Then the quadratic

temperature dependence of M_s will be altogether absent and there will be a fairly wide range of temperatures $0 < \kappa T \ll \varepsilon_{j0}$ in which M_s is practically independent of temperature (for $\kappa T < \varepsilon_{j0}$, the temperature dependence of M_s disappears exponentially on cooling). It is possible that this particular case is met with in some orthoferrites, for which $M_s(T)$ is almost constant over a wide range of temperatures [119].

3. DISCUSSION OF THE PROPERTIES OF ACTUAL ORTHORHOMBIC CRYSTALS

Rare-earth orthoferrites form a large group of orthorhombic weakly ferromagnetic crystals (orthorhombic distortion of the perovskite structure). They are compounds of the $R\text{FeO}_3$ type, where R ranges over the whole rare-earth element series (the lanthanum group). Iron may be replaced by vanadium or chromium, and the rare-earth metal may be replaced by yttrium. Since our discussion was based on the assumption that there is only one system of crystallographically equivalent sites, it applies only to the case when R^{3+} ions have no magnetic moment (for example, lanthanum, lutetium, or yttrium ions).

However, even in the case of magnetic rare-earth ions above a certain temperature (of the order of 10°K) only the Fe^{3+} ions form a magnetically ordered structure and the rare-earth ions form a disordered paramagnetic subsystem. Therefore, if the magnetic susceptibility of the paramagnetic subsystem is sufficiently low, we can neglect the influence of the rare-earth ions on the magnetic properties of orthoferrites above the temperature just mentioned, and consider only the properties connected with the subsystem of iron ions whose magnetic moments are in approximate antiferromagnetic order (Néel's point at 700°K).

The influence of the rare-earth ions on the magnetic properties above their spin-ordering temperature may be allowed for approximately by the molecular field method, considering these ions as a paramagnetic subsystem which interacts with the weakly ferromagnetic subsystem of the iron ions. This will be undertaken next.

The crystal symmetry of orthoferrites is represented by the space group D_{2h}^{16} , discussed in Sec. 2 of Chap. V (Fig. 7a). The iron ions occupy fourfold positions of the b type, which coincide with inversion centers. In our chosen coordinate system (taken from the space group table in [107], cf. Fig. 7a) the coordinates of these ions are:*

$$1(0, 0, 1/2); \quad 2(0, 1/2, 1/2); \quad 3(1/2, 1/2, 0), \quad 4(1/2, 0, 0).$$

*We note that in [38, 39, 96] a different system of coordinate axes was selected by the substitution $X \rightarrow Y$, $Y \rightarrow Z$ and $Z \rightarrow X$.

Magnetic moments occupying the b -type positions of the D_{2h}^{16} group may give rise to all three structures with weak ferromagnetism listed in Table 3. The neutron diffraction studies of Koehler et al. [120] have shown that, in the majority of cases, orthoferrites exhibit state II ($l_s \parallel Y, m_s \parallel X$) of the $2_x^+ 2_z^-$ structure ($S_1 \parallel S_3$ and $S_2 \parallel S_4$). Theoretical curves for the magnetization along the principal axes of a crystal at $T \rightarrow 0^\circ\text{K}$ are given for this case in Fig. 20. All that is needed is to make the cyclic substitution of the coordinate axes: $(XYZ) \rightarrow (YZX)$.

Unfortunately, at present, it is not possible to compare in detail the theoretical conclusions with experiment because the experimental data on the magnetization anisotropy of single-crystal orthoferrites in the region of the existence of weak ferromagnetism are very scarce. However, the theoretical conclusion that the spontaneous moment is stable under rotation by an external field is confirmed, for example, by the experiments of Gilleo [121], who detected no perceptible rotation of M_s in single crystals of GdFeO_3 subjected to fields up to 12 kilooersteds. Similarly, Belov, Zaytseva, and Kadomtseva [101] failed to reverse the magnetization of another orthoferrite LaFeO_3 (i.e., to reverse the sign of the magnetization of a sample cooled in an external field) even in fields up to 20 kilooersteds. It would be desirable to record the magnetization curves of single-crystal orthoferrites in still stronger fields ($\gtrsim 10^5$ oersteds), using pulse devices if necessary.

The temperature dependence of the spontaneous magnetization of orthoferrites has not been studied in sufficient detail to make it possible to compare it with the theory. In several orthoferrites (including orthoferrites with magnetic rare-earth ions) the spontaneous magnetization depends very weakly on temperature over a wide range of temperatures [119]. It is possible that this is the range of temperatures in which $\kappa T \ll \varepsilon_{j0}$. In some orthoferrites (for example HoFeO_3) the ordering of the magnetic moments of the rare-earth ions* which occurs on cooling gives rise to a strong increase of the spontaneous magnetic moment. Sometimes this increase of M_s may be explained by the additional appearance of "weak ferromagnetism" in the rare-earth ion system itself. Since the exchange forces responsible for the ordering of the magnetic moments of these ions are relatively weak (this is indicated by the low ordering temperature) the value of the weak ferromagnetic moment of the rare-earth ions may be considerably greater than that of the iron ions. A logical discussion of the properties of orthoferrites with allowance for the magnetic ordering of rare-earth

*The ordering of the magnetic moments of Ho^{3+} ions in holmium orthoferrite occurs at about 6.5°K .

ions requires the introduction of a large number (four or eight) magnetic sublattices with strongly noncollinear magnetic moments. An attempt to give such a treatment was made by Naish and Turov [39]. In this work (the main part of which will not be considered here), crystal symmetry was used to describe some of the observed magnetic properties of holmium and erbium orthoferrites at helium temperatures and to explain the magnetic structure of these orthoferrites as established by neutron diffraction [122].

The rare-earth magnetic ions, even above their spin-ordering temperature, may (due to an exchange interaction with the iron ions) sometimes influence strongly the temperature dependence of the spontaneous magnetization of orthoferrites. This may be taken into account by using the molecular field approximation, considering the R ions as a paramagnetic subsystem.

We shall introduce the energy of the exchange interaction between the Fe ions (with magnetization M_F) and the R ions (with the magnetization M_R):

$$E_{FR} = -I_{FR}M_F M_R. \quad (8.20)$$

Then the magnetizations of the two subsystems are given by the relationships:

$$M_F = \chi_{\perp} (H_D + H_F), \quad (8.21)$$

$$M_R = \chi_p H_R, \quad (8.22)$$

where χ_{\perp} is the transverse antiferromagnetic susceptibility of the Fe-ion subsystem, H_D is the Dzyaloshinskiy field acting on the magnetic moments of this subsystem,* χ_p is the paramagnetic susceptibility of the R-ion subsystem, and H_F and H_R are the molecular fields acting, respectively, on the Fe-ion and R-ion subsystems (these fields are due to the R-ion and Fe-ion subsystems, respectively). According to (8.20), these fields are

$$H_F = I_{FR}M_R, \quad H_R = I_{FR}M_F. \quad (8.23)$$

The susceptibility χ_p in the region of validity of the Curie-Weiss law is

$$\chi_p = \frac{S+1}{3S} \frac{\mu_R M_{0R}}{k(T - \Theta_R)}, \quad (8.24)$$

*For state II of the Fe-ion subsystem, this field is, according to (8.2), $H_D \simeq M_{0F} \bar{d}_1 / A$, where M_{0F} is the maximum possible magnetization of this subsystem at complete saturation.

where M_{OR} is the saturation magnetization and Θ_R is the paramagnetic Curie point* of the R ions, and S and μ_R are, respectively, the spin and magnetic moment of each of these ions. Having found from (8.21), (8.22), and (8.23), the values of M_F and M_R , we can then determine the total spontaneous magnetization of the whole system

$$M_s = M_F + M_R = \frac{\chi_{\perp} H_D (1 + \chi_p I_{FR})}{1 - \chi_p \chi_{\perp} I_{FR}^2}. \quad (8.25)$$

If we neglect the second term in the denominator, bearing in mind that $\chi_{\perp} I_{FR} \approx \frac{I_{FR}}{A} \ll 1$ (although we can also have $\chi_p I_{FR} \sim 1$) we obtain from (8.25)

$$M_s = \chi_{\perp} H_D (1 + \chi_p I_{FR}). \quad (8.26)$$

It is interesting to note that the second term in (8.26), representing the magnetic moment induced in the R-ion subsystem by the weak ferromagnetic moment of the Fe-ion subsystem, may be greater than the first term (which represents the inducing moment) at sufficiently low temperatures but still within the range of validity of the Curie-Weiss law for R ions. This will occur if

$$|\chi_p I_{FR}| > 1,$$

which may be compatible with the conditions of applicability of the Curie-Weiss law ($\kappa T \gg \mu_R H_R$, $\kappa \Theta_R$), because $M_{OR} \gg M_F$. The second term in (8.26) may strongly affect the temperature dependence of the spontaneous magnetization of an orthoferrite even if it is small compared with the first because of the strong (hyperbolic) temperature dependence of χ_p given by (8.24). If in the range of temperatures considered here, $|\chi_p I_{FR}| \sim 1$ and the exchange parameter I_{FR} is negative, we may have a phenomenon similar to the compensation of the magnetic moment in ferrites. The compensation temperature is now given by the relationship

$$\chi_p I_{FR} + 1 = 0. \quad (8.27)$$

Experiments on orthoferrites have shown an apparent hyperbolic rise of the spontaneous magnetization on cooling, and its disappearance at a certain temperature [119]. However, to find

*According to the Curie-Weiss theory

$$\Theta_R = \frac{S+1}{3S} \frac{\mu_R M_{OR} I_{RR}}{\kappa},$$

where I_{RR} is the exchange interaction constant for R ions.

how far these phenomena are related to the effect of magnetizing forces on the paramagnetic R-ion system, further experimental studies are needed.

Let us now consider orthorhombic crystals of MnP structure. This compound has a spontaneous magnetic moment (extrapolated to $T = 0^\circ\text{K}$) of about $1.2\mu_B$ per manganese atom. On the other hand, measurements in the paramagnetic region (using the Curie-Weiss law for the paramagnetic susceptibility) yield a value for the atomic magnetic moment of about $3.7\mu_B$, close to the theoretical value of $4\mu_B$, for manganese in the form of Mn^{3+} ions. Using this observation together with the analysis of the variation of the magnetic properties of several compounds of the MnX type (where $X \equiv \text{Bi, Sb, As, and P}$), Guseynov and Turov [37] suggested that the spontaneous magnetic moment of MnP may be of "weakly ferromagnetic" origin. A similar conclusion concerning the non-collinear distribution of the magnetic moments of the sublattices in MnP was reached earlier by Fakidov and Krasovskiy [123] from the results of their experimental investigation of the temperature dependence of the spontaneous magnetization and the magnetocaloric effect near the Curie point.

The crystal lattice of MnP, like the orthoferrite lattices, has symmetry of the space group D_{2h}^{16} , with the manganese atoms occupying fourfold-type positions in the mirror plane σ_y (Fig. 7a):*

$$\begin{array}{lll} 1 (x, 1/4, z); & 2 (\bar{x}, \bar{y}, 3/4); & 3 (1/2 + x, 1/4, 1/2 - z); \\ & 4 (1/2 - x, 3/4, 1/2 + z). \end{array}$$

According to the "parity condition" and Table 3, the only structure in which weak ferromagnetism may exist is that where $S_1 \parallel S_2$ and $S_3 \parallel S_4$ (the $2_y^+ 2_z^-$ structure).

In order to apply our theoretical results for orthorhombic weak ferromagnets with the $2_y^+ 2_z^-$ structure (Sec. 1 and 2) to the $2_y^+ 2_z^-$ structure, it is necessary to use a different coordinate notation, assuming that the Z axis lies along the orthorhombic c axis, which in this case is perpendicular to a mirror symmetry plane (the remaining axes are altered automatically by cyclic substitution) [125]. Then the conclusions which follow from the hypothesis of the noncollinear origin of ferromagnetism in MnP, and which require experimental verification may be formulated as follows.

a) The magnetic moments of manganese ions below the Curie point should lie in the $[001]$ plane (i.e., in a mirror-reflection

*We note that the same positions are occupied by rare-earth ions in orthoferrites.

plane), forming two magnetic sublattices in such a way that a single sublattice contains moments related by an inversion center. The angle between the magnetic moments of the sublattices should be about 145° (if the spontaneous antiferromagnetic axis coincides with the orthorhombic axes $[100]$ or $[010]$, so that weak ferromagnetism is purely transverse). This conclusion may be checked directly by neutron diffraction studies of the magnetic structure.

b) The noncollinearity of the magnetic moments of the sublattices should give rise to a finite and easily detected intrinsic susceptibility (of the order of χ_\perp for an antiferromagnet) at low temperatures right down to absolute zero. Therefore, it would be very interesting to investigate the magnetization curves (even those of polycrystalline samples) in strong and very strong magnetic fields.

c) Investigation of the magnetic properties of single-crystal MnP samples, together with the neutron diffraction studies of the structure, would be another direct method of checking our suggestion about the nature of ferromagnetism in this compound. The magnetization curves should differ strongly in shape for different directions of the magnetic field.

d) The temperature dependence of the spontaneous magnetization at low temperatures should not follow the $T^{3/2}$ law, as in normal ferromagnets, but the T^2 law (which may become exponential at very low temperatures). This theoretical conclusion is in agreement with the experimental measurements of Guiland [126], except that these measurements were carried out down to the temperature of liquid nitrogen only (the Curie point of MnP is 298°K). Therefore, a more accurate check of the theory requires the extension of these measurements to lower temperatures.

CHAPTER IX

Magnetic Resonance in Weak Ferromagnets

Magnetic resonance investigations are the most direct way of establishing the main properties of weakly ferromagnetic crystals compared with antiferromagnets and normal ferromagnets. Together with static magnetic measurements, magnetic resonance makes it possible, in practice, to determine all the physical parameters of a weak ferromagnet. To facilitate the easy comparison of the resonance properties of various types of weakly ferromagnetic structure, we shall devote the present chapter to this problem.

1. RESONANCE FREQUENCIES FOR VARIOUS TYPES OF WEAKLY FERROMAGNETIC STRUCTURE

We shall again begin our discussion with structures even with respect to the principal axis in a uniaxial crystal ($n_z^+ 2_d^-$). If we neglect the magnetic energy invariants of an order higher than the second, the uniform oscillation frequencies $\omega_j = \varepsilon_{j0}/\hbar$ for all such structures have, according to (6.12), the following general form (for $H \ll H_E$):

$$\omega_1 = \gamma_{\perp} [H \sin \psi (H \sin \psi + \bar{H}_D)]^{1/2}, \quad (9.1)$$

$$\omega_2 = \gamma_{\perp} \left[H_{EA}^2 + H \sin \psi \cdot \bar{H}_D + \left(\frac{\gamma_z}{\gamma_{\perp}} \right)^2 H^2 \cos^2 \psi \right]^{1/2}, \quad (9.2)$$

where $\gamma_{\perp} = \mu_{\perp}/\hbar$, $\gamma_z = \mu_z/\hbar$. and ψ is the angle between H and the principal axis.

Thus, here, as in the corresponding cases of uniaxial antiferromagnets [formulas (4.30) and (4.40)], there is one "low"

resonance frequency (ω_1) convenient for studies in the centimeter range of electromagnetic waves, while the other frequency (ω_2) is usually in the far infrared. However, the field dependence of ω_1 for magnetization in the basal plane ($\psi = \pi/2$) is, in fact, identical with the field dependence of the resonance frequency given by (2.21) for a uniaxial ferromagnet (for which the axis of easy magnetization also lies in the basal plane). The only difference is that in the present case the role of the uniaxial magnetic anisotropy field H_A is played by the effective Dzyaloshinskiy field H_D . On magnetization along the crystal axis, both frequencies, ω_1 and ω_2 are identical with the resonance frequencies of a normal antiferromagnet. This is yet another manifestation of the anisotropy of weak ferromagnetism: the weak ferromagnetism is in the basal plane and the normal antiferromagnetism is along the principal axis.

The resonance frequencies ω_1 and ω_2 are independent, according to (9.1) and (9.2), of the direction of H in the basal plane. As in the case of the static properties, the anisotropy of ω_1 and ω_2 in the basal plane of the n^+2^- -type structures appears only because of higher-order terms in the magnetic energy expression. The appropriate formulas have been obtained only for trigonal crystals [formulas (6.27)]. One of the frequencies, ω_1 , is governed by the transverse component of the field $H_- = H \sin \psi$.

Tetragonal Crystal Structure Odd with Respect to the Principal Axis ($4_z^-2_d^+$)

The resonance frequencies as well as the static properties of this structure depend, in general, in a very complex way on the magnitude and direction of the field. Therefore, the features of this structure will be illustrated using the following simple special cases representing the spontaneous weak ferromagnetic states Π_1 and Π_2 (Chap. VII, Sec. 1).

1) The Π_1 state, $H_- \parallel m_s \parallel M_s \perp l_s$.

When the longitudinal component of the field is $H_z = H \cos \psi$, we have, instead of (7.40),

$$\omega_1 = \gamma_{\perp} [(H_{EA}^{(1)})^2 + H^2 \sin^2 \psi + (\bar{H}_D + 4H_D) H \sin \psi]^{1/2}, \quad (9.3)$$

$$\omega_2 = \gamma_{\perp} \left[(H_{EA}^{(2)})^2 + \left(\frac{\gamma_z}{\gamma_{\perp}} \right)^2 H^2 \cos^2 \psi + \bar{H}_D H \sin \psi \right]^{1/2}, \quad (9.4)$$

where

$$H_{EA}^{(2)} = \frac{V \sqrt{Ab + d^2}}{M_0 g_{\perp}}, \quad H_{EA}^{(1)} = \frac{V \sqrt{Af + 4d^2}}{M_0 g_{\perp}}.$$

Here again, the resonance frequency ω_1 is governed only by the transverse component of the field. In contrast to structures of

the $n^+2_d^-$ type, allowance for the g -factor anisotropy ($\tau \neq 0$) cannot now be reduced to a simple renormalization of the Dzyaloshinskiy field H_D : we must use two parameters to represent the weak ferromagnetism— H_D and \bar{H}_D (or H_D and τ). Another characteristic feature is the shift of the resonance frequency ω_1 by the effective magnetic anisotropy fields, i.e., the quantity

$$\left(\frac{\omega_1}{\gamma_1}\right)_{H \rightarrow 0} = H_{EA}^{(4)} - \sqrt{H_E H_A^{(4)} + 4H_D^2} \quad (9.5)$$

does not vanish in the case of tetragonal odd structures even if we neglect the usual magnetocrystalline anisotropy of antiferromagnets in the basal plane ($H_A^{(4)} = 0$). In this case, the shift will be determined by the Dzyaloshinskiy field H_D . The order of magnitude of $H_{EA}^{(4)}$ may reach 10^3 – 10^4 oersteds. The second resonance frequency ω_2 , given by (9.4), does not differ in any way from the corresponding frequency given by (9.2) for structures of the $n^+2_d^-$ type.*

2) The state Π_2 , $H \parallel M_s \parallel l_s$.

The general expressions for the resonance frequencies of this state may be derived from the general formulas for ε_{jk} [cf. the second footnote after (7.47)]. We shall give these expressions only for the special case when we can neglect all the “magnetic” parameters ($a = b = d = f = 0$) except parameter τ , responsible for the longitudinal weak ferromagnetism. For this case, we obtain from (7.49)

$$\omega_{1,2} = \gamma_{\perp} (\sqrt{\tau H_E H} \pm H). \quad (9.6)$$

Thus, even this special case shows that the dependence of the resonance frequencies on the external magnetic field for longitudinal weak ferromagnetism is of a completely different nature than that for the transverse case [compare (9.6) with (9.3) and (9.4) for $\psi = \pi/2$].

*We note that formulas (9.3) and (9.4) are easily generalized to the case of an arbitrary direction of H , provided $\tau = 0$ and $H_{\perp} \gg H_{EA}^{(4)}$, i.e., under these conditions ($M_{\perp} \parallel H_{\perp}$) we have, in place of (9.3) and (9.4)

$$\omega_1 = \gamma_{\perp} [H_E H_A^{(4)} \cos 4\varphi_H + (H \sin \psi + H_D \cos 2\varphi_H) (H \sin \psi + 4H_D \cos 2\varphi_H)]^{1/2},$$

$$\omega_2 = \gamma_{\perp} [H_E (H_A^{(2)} - \frac{1}{2} H_A^{(4)} \sin^2 2\varphi_H) + H_D \cos 2\varphi_H (H \sin \psi +$$

$$+ H_D \cos 2\varphi_H) + \left(\frac{\gamma_z}{\gamma_{\perp}}\right)^2 H^2 \cos^2 \psi]^{1/2}.$$

Here, angle φ_H should be taken from the nearest side of the basal square if the state considered is obtained in such a way that it represents an absolute energy minimum (cf. Chap. VII, Sec. 1).

Hexagonal Crystal Structures Odd with Respect to the Principal Axis ($6_z^- 2_d^+$)

For these structures, we shall enumerate the resonance frequencies for the longitudinal magnetization case ($H \parallel Z$).

In the weak ferromagnetic state ($l \perp Z$, $\cos 3\varphi = 0$) when $H \parallel Z$, we have, according to (7.61):

$$\omega_1 = 3\gamma \sqrt{H_t (H_{te} + H)}, \quad (9.7)$$

$$\omega_2 = \gamma \sqrt{H_{EA}^2 + (H + 5H_t) H}, \quad (9.8)$$

where

$$H_t = \frac{t}{M_0 g}, \quad H_{EA} \simeq \frac{\sqrt{Ab}}{M_0 g} \text{ and } H_{te} = \frac{t^2 + 4eA}{tM_0 g}. \quad (9.9)$$

We note the quantity H_{te} may be positive or negative, depending on which of the states, Π_2 or Π_1 , is the spontaneous state (cf. Chap. VII, Sec. 3). If H_{te} is negative, formulas (9.7) and (9.8) are valid only if $H \geq |H_{te}|$. The order of magnitude of H_{te} may range within the limits 10^2 - 10^5 oersteds for different crystals.* It is worth noting the characteristic dependence of the lower resonance frequency ω_1 on the field for this type of weak ferromagnetism (due to fourth-order invariants) in strong fields $H \gg |H_{te}|$:

$$\omega_1 \sim \sqrt{H}.$$

In all the other cases of transverse weak ferromagnetism (due to second-order invariants), we have $\omega_1 \sim H$ in sufficiently strong magnetic fields [formulas (9.1) and (9.3)].

Orthorhombic Crystals, $2_2^+ 2_x^-$ Structure

We shall again consider only the case when $H \parallel M_s \parallel X$, $l \parallel Y$. Here, according to (8.15), we have:

$$\omega_1 = \gamma_x \sqrt{H_{EA1}^2 + H [2 (H_{D1} - H_{D2}) + \overline{H}_{D1}] + H^2}, \quad (9.10)$$

$$\omega_2 = \gamma_x \sqrt{H_{EA2}^2 + H \overline{H}_{D1}}, \quad (9.11)$$

* $H_{te} \sim \frac{e}{t} H_E \sim \frac{V_0^2}{c^2} H_E$.

where

$$H_{EA1}^2 = \frac{A(b_1 - b_2) + 2d_1(d_1 - d_2)}{M_0^2 g_{xx}^2}, \quad H_{EA2}^2 = \frac{A|b_2| + d_1^2}{M_0^2 g_{xx}^2}, \quad (9.12)$$

$$H_{Dj} = \frac{d_j}{M_0 g_{xx}}, \quad \bar{H}_{D1} = H_{D1} + \tau_1 H_E. \quad (9.13)$$

Both resonance frequencies should now lie in the far-infrared region (or, at best, in the millimeter region).

From expressions (9.10) and (9.11), we may obtain the resonance frequencies of uniaxial crystals if the terms of second order in m and l are neglected in the magnetic energy expression:

1) if we assume that $b_1 = b_2$ and $d_1 = d_2$, we obtain formulas (9.1) and (9.2) for structures of the $n_z^+ 2_d^-$ type (for the case $\psi = \pi/2$);

2) if we assume that $b_1 = b_2$ and $d_1 = -d_2$, we obtain formulas (9.3) and (9.4) for structures of the $4_z^- 2_d^+$ type (again for $\psi = \pi/2$).

2. HIGH-FREQUENCY MAGNETIC SUSCEPTIBILITY AND RESONANCE CONDITIONS

To observe magnetic resonance, it is necessary to know not only the resonance frequency but also the direction of the high-frequency magnetic field h_ω capable of exciting oscillations at the resonance frequency ("selection rules"). In contrast to normal antiferromagnetism (Chap. IV, Sec. 3), we shall here obtain these rules by solving the classical equations of motion

$$\frac{d\mathbf{M}_j}{dt} = -\gamma [\mathbf{M}_j \cdot \mathbf{H}_j] - \gamma \frac{\lambda}{M_0} [\mathbf{M}_j [\mathbf{M}_j \cdot \mathbf{H}_j]]. \quad (9.14)$$

Here,

$$\mathbf{H}_j = -\frac{\partial \mathcal{H}(r)}{\partial \mathbf{M}_j} (\mathcal{H}_{\text{inhom}} = 0),$$

and, for simplicity, we shall restrict our discussion to the case when the g factor is isotropic ($\gamma = ge/2mc$). The second term in (9.14) allows phenomenologically (according to Landau and Lifshits [15]) for the processes of the damping of the oscillations of \mathbf{M}_j ; λ is a dimensionless damping parameter.

To deduce the resonance conditions, we shall first assume that $\lambda = 0$. We shall deal with orthorhombic weak ferromagnets. For these, the uniaxial structures (both even and odd with respect to the principal axis) are special cases if the magnetic energy

is restricted to terms not higher than the second order in M_j (or in $M = M_1 + M_2$ and $L = M_1 - M_2$).

Let us assume that the system considered is placed in a steady magnetic field $H \parallel M_s \parallel X$. According to Sec. 1 of Chap. VIII, at equilibrium $M^{(0)} \parallel X$ and $L^{(0)} \parallel Y$ (the state II of an orthorhombic weak ferromagnet), and when $H \ll H_E$

$$M^{(0)} = \chi_{\perp} (H_{D1} + H) \text{ and } L^{(0)} \simeq gM_0. \quad (9.15)$$

We shall now assume that, apart from a steady field, a uniform high-frequency magnetic field

$$h_{\omega} = h_0 \cdot e^{i\omega t}$$

of arbitrary direction but small amplitude is applied so that it causes only weak forced oscillations of the vectors M and L (or the related vectors M_1 and M_2) about their equilibrium values $M^{(0)}$ and $L^{(0)}$:

$$\Delta M = M - M^{(0)}, \quad \Delta L = L - L^{(0)}.$$

Changing in (9.14) from M_j to L and M , and linearizing the latter with respect to ΔM and ΔL , we can easily find the high-frequency component of the total magnetization:

$$\Delta M_{\alpha} = \chi_{\alpha\beta} h_{\omega\beta}. \quad (9.16)$$

The magnetic susceptibility related to the high-frequency field h_{ω} (the high-frequency susceptibility) has the following form

$$\chi_{\alpha\beta} = \begin{vmatrix} \chi_{xx} & 0 & 0 \\ 0 & \chi_{yy} & \chi_{yz} \\ 0 & \chi_{zy} & \chi_{zz} \end{vmatrix}, \quad (9.17)$$

where

$$\begin{aligned} \chi_{xx} &= \chi_0 \frac{\omega_2^2}{\omega_2^2 - \omega^2}, \quad \chi_{yy} = \chi_0 \frac{\gamma^2 (H + H_{D1})^2}{\omega_1^2 - \omega^2}, \\ \chi_{zz} &= \chi_0 \frac{\omega_1^2}{\omega_1^2 - \omega^2}, \quad \chi_{yz} = -\chi_{zy} = i\chi_0 \frac{\omega\gamma (H + H_{D1})}{\omega_1^2 - \omega^2}, \end{aligned} \quad (9.18)$$

$\chi_0 \equiv \chi_{\perp}$ is the transverse static susceptibility of an antiferromagnet, and ω_1 and ω_2 are the resonance frequencies given by (9.10) and (9.11).

Thus, when the directions of the magnetization and the steady magnetizing field are identical, we have, as in the case of transversely magnetized normal antiferromagnets, oscillations of one frequency (ω_1) which may be excited by the high-frequency field $h_\omega \perp H$, and oscillations of another frequency (ω_2) which may be excited by the field $h_\omega \parallel H$. The difference between the high-frequency susceptibility tensor for a weak ferromagnet and the corresponding tensor for an antiferromagnet is merely the addition of the Dzyaloshinskiy field H_{D_1} to the external field H in the formulas for χ_{yy} and χ_{yz} .

In the case of uniaxial weak ferromagnets of the $n_z^+ 2_d^-$ (where $n = 3, 4$, and 6) and $4_z^- 2_d^+$ -type structures, the tensor is still given by (9.17), with the same expressions (9.18) for the non-zero components. All that is necessary is to take the resonance frequencies ω_1 and ω_2 which correspond to these structures.

For these structures in uniaxial crystals, the oscillations of the lower ("radiospectroscopic") frequency should be excited by a transverse high-frequency field ($h_\omega \perp H$).

The formulas (9.18) can be used also to deduce the "selection rules" for resonance in weak ferromagnets of the $6_z^- 2_d^+$ -type structure, in which the spontaneous magnetic moment is due to magnetic-energy terms of order higher than the second (cf. Chap. VII, Sec. 3). If these terms are ignored, then in the case of magnetization along the hexagonal axis we have the special case of orthorhombic crystals for

$$d_1 = d_2 = b_2 = a_2 = 0,$$

where the role of the hexagonal axis Z is played by the X axis, and the lower frequency ω_1 [formula (9.7)] becomes the frequency ω_2 of an orthorhombic crystal [formula (9.11)]. This means that the lower frequency oscillations in the $6_z^- 2_d^+$ structures should be, in contrast to all other cases, excited not by a transverse but by a longitudinal high-frequency field ($h_\omega \parallel H \parallel M_s$).

We shall now consider the high-frequency susceptibility making allowance for damping. We shall discuss this for the case of the $n_z^+ 2_d^-$ structures; but for the other structures, the main results will be the same. We shall again calculate the small forced oscillations of M and L near the ground state $M^{(0)} \parallel H \parallel X$ and $L^{(0)} \parallel Y$, using for this purpose the Hamiltonian (6.1) (for $\mathcal{H}_{\text{inhom}} = 0$) and the equations

*We are speaking here only of transverse weak ferromagnetism because (9.14) with an isotropic g factor is not valid in the case of longitudinal weak ferromagnetism. It is easily found that both frequencies given by (9.6) for longitudinal weak ferromagnetism are excited when $h_\omega \perp l$, as in the case of normal antiferromagnets when $H \parallel l$.

(9.14), allowing for the damping terms. In this way, we obtain for the high-frequency susceptibility a tensor of the (9.17) type with the following components:

$$\begin{aligned}\chi_{xx} &= \chi_0 \frac{\omega_2^2 p^2 + i\omega\lambda\gamma H_E}{\omega_2^2 p^2 - \omega^2 + i\omega\lambda\gamma H_E}, \quad \chi_{yy} = \chi_0 \frac{\gamma^2 (H + H_D)^2 p^2}{\omega_1^2 p^2 - \omega^2 + i\omega\lambda\gamma H_E}, \\ \chi_{zz} &= \chi_0 \frac{\omega_1^2 p^2 + i\omega\lambda\gamma H_E}{\omega_1^2 p^2 - \omega^2 + i\omega\lambda\gamma H_E}, \\ \chi_{yz} &= -\chi_{zy} = i\omega\chi_0 \frac{\gamma (H + H_D)}{\omega_1^2 p^2 - \omega^2 + i\omega\lambda\gamma H_E},\end{aligned}\tag{9.19}$$

where

$$\omega_1 = \gamma \sqrt{H(H + H_D)}$$

and

$$\omega_2 = \gamma \sqrt{H_{EA}^2 + HH_D}, \quad p = 1 + \lambda^2.$$

Separating $\chi_{\alpha\beta}$ into its real and imaginary components: $\chi_{\alpha\beta} = \chi'_{\alpha\beta} - i\chi''_{\alpha\beta}$, we can find the resonance linewidth $\Delta\omega$ as a range of frequencies (on both sides of resonance) for which $\chi''_{\alpha\alpha}$ is half its maximum value. Assuming that $\Delta\omega \ll \omega$, we obtain for both oscillation modes a linewidth given by the same relationship

$$\Delta\omega = \lambda\omega_E,\tag{9.20}$$

which applies to normal antiferromagnets [127] (here, $\omega_E = \gamma H_E$ is the frequency representing the exchange field). Apart from broadening the resonance curve, damping also displaces the resonance frequencies, so that according to (9.19)

$$\omega_{j\text{res}} = \omega_j (1 + \lambda^2).$$

Guseynov [128] has shown that the formula (9.20) for $\Delta\omega$ retains the same form when the steady magnetizing field is directed at any angle ψ to the principal axis of a crystal; consequently, if an equation of the (9.14) type describes correctly the relaxation in antiferromagnets, the linewidth $\Delta\omega$ should be independent of the angle ψ . We must stress that we are speaking here of the linewidth on the frequency scale (for constant H). The linewidth on the field scale (for constant ω) will depend in some way on ψ (cf. Sec 3).

It is characteristic of normal ferromagnets that a completely different relationship is obtained for the linewidth defined in the same way. Instead of (9.20), we then have $\Delta\omega = \lambda\omega_{\text{res}}$, which differs from (9.20) in that instead of the exchange frequency ω_E ,

we have the resonance frequency ω_{res} . Consequently, if the damping parameter λ of antiferromagnets (and weak ferromagnets) has the same nature and the same order of magnitude as in ferromagnets, the linewidth for the former should be several orders of magnitude greater than that for the latter. So far, practically no experimental work has been done on the linewidth of antiferromagnets and weak ferromagnets; the linewidth of various ferromagnets ranges between very wide limits ($\Delta H \sim 10^{-1} 10^3$ oersteds [24]). Therefore, we cannot yet say whether the suggested relationship between the linewidths of ferromagnets and antiferromagnets is valid.

From the theoretical point of view, it would be very interesting to deal with the problem of the form of the equations of motion for magnetic moments in antiferromagnets and weak ferromagnets on the basis of the transport equations for spin waves, which would allow both for collisions between spin waves and for their scattering on phonons, crystal-lattice defects, etc. Such studies for ferromagnets have been carried out by Akhiezer, Kaganov, and Bar'yakhtar [17], and Gurzhi and Tsukernik [129], etc.

3. DISCUSSION OF THE EXPERIMENTAL DATA ON THE RESONANCE IN HEMATITE AND MANGANESE CARBONATE

Experimental investigations of the magnetic resonance in weak ferromagnets have been carried out by Anderson et al. [130] and Kumagai et al. [131] on hematite ($\alpha\text{-Fe}_2\text{O}_3$), and by Date [132] and Borovik-Romanov [133] on manganese carbonate (MnCO_3). Both these compounds have the weakly ferromagnetic structure $3_2^+ 2_2^-$. These workers investigated the dependence of the lower resonance frequency ω_1 (in the centimeter region) on the magnitude and direction of the field H . The resonance-frequency oscillations were excited by a high-frequency field applied at right angles to the planes containing M and H .

The dependence of the resonance frequency ω_1 on the field H and the angle ψ which this field makes with the trigonal axis are given by (9.1). However, since in these experiments a given frequency ω was kept constant and the field H was usually varied, (9.1) should be rewritten in the form

$$H = \frac{H_{\perp}}{\sin \psi}, \quad (9.21)$$

where

$$H_{\perp} = \sqrt{\left(\frac{\bar{H}_D}{2}\right)^2 + \left(\frac{\omega_1}{\gamma_{\perp}}\right)^2} - \frac{\bar{H}_D}{2} \quad (9.22)$$

is the resonance field for $H \perp Z$ (i.e., for $\psi = \pi/2$). The relationship (9.21), which gives the dependence of the resonance field magnitude on its direction in a vertical plane at a constant frequency ω_1 , is in excellent agreement with the experimental data both on $\alpha\text{-Fe}_2\text{O}_3$ [131] and on MnCO_3 [132, 133].

The agreement is somewhat poorer in the case of the dependence of H_\perp and ω_1 since instead of (9.22) the experiments gave for both compounds a nearly linear dependence. In not too weak fields ($H > 1\text{--}2$ kilooersteds) the agreement of theory with experiment in the case of hematite may be improved by including in the magnetic energy the anisotropy terms of order higher than the second. If such terms are included, then, using the first of the formulas in (6.27), instead of (9.22) we have approximately

$$H_\perp = \sqrt{\left(\frac{\bar{H}_D}{2}\right)^2 + \left(\frac{\omega_1}{\gamma_\perp}\right)^2} - \frac{1}{2} \left[\bar{H}_D + \frac{H_\Delta^2 \cos 6\varphi_H}{\sqrt{\left(\frac{\bar{H}_D}{2}\right)^2 + \left(\frac{\omega_1}{\gamma_\perp}\right)^2}} \right], \quad (9.23)$$

where

$$H_\Delta^2 = 36A \left(e - \frac{q^2}{b} \right) / M_0^2 g_\perp^2.$$

According to the data [130, 131] on hematite, small periodic variations of the resonance field were found when it was rotated in the basal plane, so that $H_\perp = \text{const} + C \cos 6\varphi_H$ (where the amplitude was $C \lesssim 10^2$ oersteds). Thus, the resonance formula (9.23) contains two parameters: \bar{H}_D and H_Δ (if we ignore the g factor, which is assumed to be equal to 2). These parameters may be selected to obtain the best agreement between the theory and experiment for the dependence of H_\perp on ω_1 . Figure 22 shows the theoretical curve for the relationship between $1/\lambda_1 = \omega_1/2\pi c_0$ and the resonance field H_\perp , which is directed along the "easy axis" X [corresponding to $\cos 6\varphi_H = 1$ in formula (9.23)] when $\bar{H}_D = 22,800$ oersteds and $H_\Delta = 1,450$ oersteds.* The points in Fig. 22 represent the experimental data [131].

*These values of \bar{H}_D and H_Δ are in good agreement with the observed amplitude of the resonance-field oscillation when it is rotated in the basal plane; this is easily checked using

$$C = \frac{1}{2} \frac{H_\Delta^2}{\left(\frac{\bar{H}_D}{2}\right)^2 + \left(\frac{\omega_1}{\gamma_\perp}\right)^2}.$$

Figure 22 indicates completely satisfactory agreement between the theory and experiment, with the exception of weak fields. Obviously, because of the presence of various crystal defects and antiferromagnetic domains, the magnetization is not saturated in fields $H_{\perp} \lesssim 2$ kilooersteds. The magnetization curves obtained by other workers [134], indicate that the saturation in the basal plane is not reached in fields up to 1-2 kilooersteds, although, according to (6.25), in an ideal crystal saturation should occur in fields as low as

$$H > H^* = \frac{H_{\Delta}^2}{H_D} \sim 100 \text{ oersteds.}$$

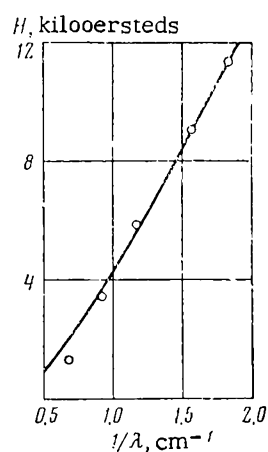


Fig. 22

Satisfactory agreement between the theoretical and experimental dependence of \bar{H}_{\perp} on ω_1 [132] can be obtained also for MnCO_3 by a suitable selection of the parameters H_D and H_{Δ} . However, the value of H_{Δ} obtained then contradicts the experimental observation of the lack of any noticeable anisotropy of H_{\perp} [133]. According to the published data, the Dzyaloshinskiy field \bar{H}_D is, respectively, 5.3 kilooersteds [133] and 3.7 kilooersteds [132]. Such a considerable difference is obviously due to the influence of impurities. This is supported by the linewidths ΔH reported in these two papers: about 10 oersteds in [133] and about 500 oersteds in [132]. The difference of more than one order of magnitude in the linewidth indicates that Borovik-Romanov [133] used purer samples.

The linewidth ΔH is related to the linewidth on the frequency scale $\Delta\omega$ by

$$\Delta H = \frac{\Delta\omega}{\frac{\partial\omega_1}{\partial H}}. \quad (9.24)$$

Therefore, the theoretical conclusion (which follows from the assumption that it is possible to represent damping in the Landau-Lifshits equation of motion) that $\Delta\omega$ is independent of the polar angle ψ in a field H should, according to (9.1), (9.20) and (9.24), lead to the following dependence of ΔH on this angle:

$$\Delta H = \frac{\Delta H_{\perp}}{\sin \psi}, \quad (9.25)$$

where

$$\Delta H_{\perp} = \frac{\lambda H_E \omega_1}{\sqrt{\omega_1^2 + \left(\frac{\gamma_{\perp} \bar{H}_D}{2}\right)^2}} \quad (9.26)$$

is the linewidth for magnetization in the basal plane. The latter formula also predicts a definite dependence of ΔH on the frequency ω_1 . It would be interesting (in order to check the validity of the Landau-Lifshits equation of motion in the case of weak ferromagnets) to investigate experimentally both these dependences of ΔH : on the angle ψ and on the frequency ω_1 . The former dependence was studied by Date [132]; very roughly it is in agreement with the theoretical formula (9.25). However, it would have been desirable to carry out measurements on samples with a narrower resonance line. It is illuminating to compare the value of the Dzyaloshinskiy field \bar{H}_D , found from resonance experiments, with its value obtained from static measurements (Chap. VI, Sec. 4). Such a comparison is made below:*

	$(\bar{H}_D)_{st}$, kilooersteds	$(\bar{H}_D)_{res}$, kilooersteds
$\alpha\text{-Fe}_2\text{O}_3$	20	22.8
MnCO_3	4.5	5.3

Thus, there is satisfactory agreement between the static and resonance data for both compounds and, according to (9.22), this agreement may be improved if we take the g factor to be greater than 2.

In conclusion, we note that it would be desirable to investigate the resonance absorption near the second frequency (ω_2), defined by (9.2). These investigations should be carried out in the far infrared. The direction of the high-frequency magnetic field h_ω should be parallel to the direction of the steady field H , if the latter lies in the basal plane, but if $H \parallel Z$, it is necessary to have $h_\omega \perp H$.

*For MnCO_3 , we took the data of Borovik-Romanov [133] as the more reliable.

CHAPTER X

Noncollinear Antiferromagnetism

In the preceding chapters dealing with weak ferromagnetism, we have allowed only for such noncollinearity of the magnetic moments as had led to the appearance of a weak spontaneous magnetic moment (as a result of the perturbing action of magnetic forces on the initially strictly antiferromagnetic structure). In other words, we have allowed only for the possibility of a departure from the collinearity of initially antiparallel magnetic moments and have ignored the possibility of noncollinearity of the magnetic moments which had initially been parallel. If the latter possibility is accommodated, in some cases magnetic forces may transform an initially collinear antiferromagnetic structure into a weakly noncollinear or even noncoplanar structure (the resultant magnetic moment may or may not be zero), which we cannot, strictly speaking, represent by means of two magnetic sublattices. We shall not deduce the general conditions for the appearance of such structures but we shall illustrate this possibility for special cases of the space groups D_{2h}^{16} and D_{2h}^{17} for the case of fourfold positions of various types.

We shall not consider at all the strongly noncollinear magnetic structures in which the noncollinearity of the magnetic moments is due to exchange forces.

1. NONCOLLINEAR AND NONCOPLANAR MAGNETIC STRUCTURES IN A SYSTEM OF FOUR MAGNETIC SUBLATTICES

We shall consider first the same fourfold positions of the D_{2h}^{16} group which we have discussed in Chap. VIII: positions of the b type (occupied, for example, by iron ions in orthoferrites)

or positions of the type c (occupied, for example, by rare-earth ions in orthoferrites, or by manganese ions in MnP). Since we are now interested not only in weakly ferromagnetic structures, but also in structures with compensated (but noncollinear) antiferromagnetism, the magnetocrystalline and crystallochemical unit cells may, in general, be different. However, for simplicity, we shall assume that they are identical, so that the number of magnetic sublattices corresponds to four magnetic atoms in a unit cell.*

We shall number the magnetizations of the sublattices in the following way:

positions b : $M_1 (0, 0, 1/2)$; $M_2 (0, 1/2, 1/2)$; $M_3 (1/2, 1/2, 0)$;
 $M_4 (1/2, 0, 0)$;

positions c : $M_1 (x, 1/4, z)$; $M_2 (\bar{x}, 3/4, \bar{z})$; $M_3 (1/2 + x, 1/4, 1/2 - z)$;
 $M_4 (1/2 - x, 3/4, 1/2 + z)$.

The coordinates of a basal site for each magnetic sublattice are given in parentheses (so that all the other sites of these sublattices may be obtained by translation to distances which are multiples of the crystal period).

We can write the density of the exchange and magnetic energies of the system in the form of an expansion in $M_j(r)$ ($j = 1, 2, 3, 4$) which is invariant under all symmetry operations of the D_{2h}^{16} group (translations are replaced with identity elements). However, this is more conveniently done by replacing M_j with new vectors M_2, L_1, L_2, L_3 using the relationships listed in Table 6.

Table 6

Type of structure	Positions b	Positions c
$(F): M = M_1 + M_2 + M_3 + M_4$ $\begin{matrix} 2 \rightarrow & \rightarrow 3 \\ 1 \rightarrow & \rightarrow 4 \end{matrix}$	$I + 2_z^+ \sigma_y^+$	$I + 2_z^+ \sigma_y^+$
$(A_1): L_1 = M_1 - M_2 + M_3 - M_4$ $\begin{matrix} 2 \rightarrow & \leftarrow 3 \\ 1 \leftarrow & \rightarrow 4 \end{matrix}$	$I - 2_z^- \sigma_y^-$	$I - 2_z^- \sigma_y^+$
$(A_2): L_2 = M_1 - M_2 - M_3 + M_4$ $\begin{matrix} 2 \leftarrow & \leftarrow 3 \\ 1 \rightarrow & \rightarrow 4 \end{matrix}$	$I + 2_z^+ \sigma_y^-$	$I - 2_z^+ \sigma_y^+$
$(A_3): L_3 = M_1 + M_2 - M_3 - M_4$ $\begin{matrix} 2 \rightarrow & \leftarrow 3 \\ 1 \rightarrow & \leftarrow 4 \end{matrix}$	$I + 2_z^- \sigma_y^+$	$I + 2_z^- \sigma_y^+$

*We are again assuming that there is only one system of crystallographically equivalent magnetic atoms, (in positions b or c).

On the right of each relationship in the first column of Table 6 there is a schematic representation of the type of ordering of the four magnetic moments for which the corresponding vector (M , L_1 , L_2 or L_3) has the maximum absolute value (when the other three vectors are equal to zero). In this way, we obtain all the possible collinear magnetic structures: one of them (F) is ferromagnetic, and the three other (A_1 , A_2 and A_3) are antiferromagnetic. The last two columns of Table 6 contain the independent symmetry elements (cf. Fig. 7a) and the parity of the listed structure with respect to these elements. Since we are now interested in all antiferromagnetic structures, including those which do not exhibit weak ferromagnetism, we must include also the structures which are odd with respect to an inversion center. In other words, for the D_{2h}^{16} group we must consider now all the possible combinations of the parities with respect to three independent symmetry elements (and not two elements, as was done in our discussion of weakly ferromagnetic structures in Chap. V). This does not give rise to new structures for the b -type positions (because inversion centers coincide with these positions) but it yields two additional antiferromagnetic structures, odd with respect to an inversion center, for positions of the c type.

Consideration of the transformation properties of the vectors M and L_i ($i = 1, 2, 3$) shows that under all the symmetry operations of the D_{2h}^{16} group these vectors transform only into themselves; it is precisely this property that makes them convenient for describing magnetic structures.

Let us assume that exchange forces give rise to one of the antiferromagnetic structures listed in Table 6. In Chap. V we have established the general conditions for the appearance of $M \neq 0$ for any vector $L_i \neq 0$. $M \neq 0$ appear when mixed terms of the $L_{i\alpha}M_\beta$ type are present in the magnetic energy. However, the magnetic energy may also include mixed invariants of the type

$$L_{i\alpha}L_{i'\beta} \ (i \neq i'). \quad (10.1)$$

This means that the magnetic ordering with $L_i \neq 0$ should give rise, under certain conditions, to $L_{i'} \neq 0$ (and conversely). Consequently, we obtain a more complex noncollinear (or even noncoplanar) structure which may be regarded as the superposition of two (or three) collinear structures listed above.

In order to obtain the invariants consisting of the vectors M and L_i , we shall write in a row the components of these vectors which transform in the same way under all symmetry operations of the lattice (it is sufficient to consider only the independent elements listed in Table 6). The result may be shown in the form used in Table 7 (first and second columns).

The third column of Table 7 refers to the b -type positions of the D_{2h}^{17} group (see below).

Table 7

Row no.	Group D_{2h}^{16}	Group D_{2h}^{16}	Group D_{2h}^{17}
	Positions b	Positions c	Positions b
1	M_z, L_{1y}, L_{3x}	M_z, L_{3x}	M_y, L_{3z}
2	M_x, L_{2y}, L_{3z}	M_x, L_{3z}	M_z, L_{3y}
3	M_y, L_{1z}, L_{2x}	M_y	M_x
4	L_{1x}, L_{2z}, L_{3y}	L_{3y}	L_{3x}
5		L_{1x}, L_{2z}	L_{1z}, L_{2y}
6		L_{1z}, L_{2x}	L_{1y}, L_{2z}
7		L_{1y}	L_{1x}
8		L_{2y}	L_{2x}

Using Table 7, we can easily write down an invariant expansion of the energy (or the thermodynamic potential) in terms of M and L_i . In particular, the second-order invariants are obtained by multiplying in pairs the components listed in the same row of Table 7, including the multiplication of each of the components by itself. The general phenomenological expression for the energy obtained in this way may, in principle, be minimized with respect to all 12 variables (or 24 variables if the magnetic atoms occupy both types of position [39]). In this way, we can find all the possible magnetic structures and states of the system considered here and the conditions necessary for obtaining them. However, some conclusions may be drawn directly from Table 7.

The quantities in the same row of Table 7 affect one another so that if one of them is not equal to zero, the other quantities appear because of the presence of mixed terms in the expression for the energy. Therefore, if the magnetic atoms occupy positions of the b type, none of the four structures listed in Table 7 can be realized in its pure form. Let us assume that, for example, exchange forces give rise to a collinear antiferromagnetic structure A_1 ($L_1 \neq 0$), and the magnetocrystalline anisotropy is such that the spontaneous antiferromagnetic axis is directed along an orthorhombic axis Z ($L_1 \parallel Z$). Then, according to the third row in

Table 7 (for positions of the b type), the perturbing action of magnetic fields should lead to the appearance of $L_{2x} \neq 0$ and $M_y \neq 0$, so that a small "admixture" of the antiferromagnetic structure A_2 and of the ferromagnetic structure F appears in the initial structure A_1 . The resultant weakly ferromagnetic structure is shown schematically in Fig. 23a, in which the magnetic moment sublattices are plotted for the same common point. Similarly, if $L_1 \parallel Y$, the resultant structure (corresponding to the first row in Table 7) may be represented as the superposition of the initial structure A_1 and the structures A_3 and F . If $L_1 \parallel X$ (i.e., if the antiferromagnetic axis of the initial structure is directed along the symmetry axis with respect to which this structure is even), then according to the fourth row in Table 7, we obtain a structure with compensated antiferromagnetism due to the superposition of all three collinear antiferromagnetic structures— A_1 , A_2 and A_3 (Fig. 23b). The three different components of the three vectors

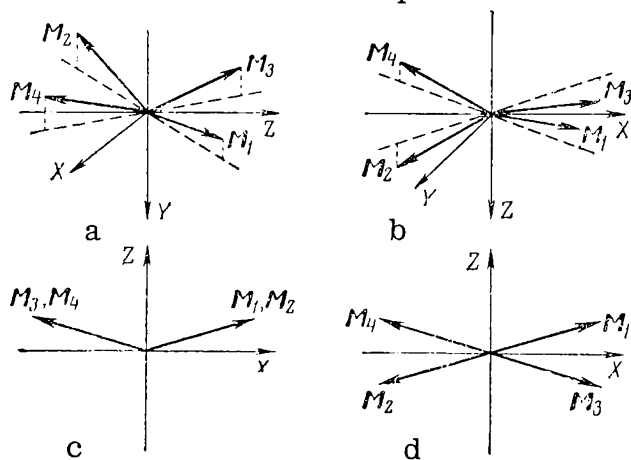


Fig. 23

for the b -type positions are always mixed and therefore the resultant structure is three-dimensional (noncoplanar). Similar noncoplanar configurations of the magnetic moments are obtained when the other antiferromagnetic structures (A_2 and A_3) are taken as the initial ones* so that in this sense all three antiferromagnetic structures may be regarded as being of equal weight.

*When exchange forces give rise to collinear ferromagnetic structure F , mixed terms of the $M_\alpha L_{i\beta}$ type in the magnetic energy should produce small deviations of the sublattice magnetic moments from strict parallelism. In this case, we have a weak "admixture" of antiferromagnetism with ferromagnetism. This may affect the following macroscopic properties: a) the nominal value of the spontaneous magnetization of a ferromagnet; b) the effective value of the g factor of an antiferromagnet; c) the intrinsic susceptibility (especially at low temperatures). These effects should, as a rule, be small because the noncollinearity of magnetic moments, due to the competition between magnetic and exchange forces, is usually slight.

The situation is different in the case of magnetic moments in positions of the c type. For these positions, the ferromagnetic vector M may be associated in the ferromagnetic energy expression with only one antiferromagnetic vector L_3 (first and second rows in Table 7). The other two vectors L_1 and L_2 may be associated only with one another (fifth and sixth rows in Table 7). Only the x and z components of these vectors are associated with one another; therefore, the magnetic structure will be noncollinear if the sublattice magnetic moments are parallel to the XZ plane, and collinear when they are perpendicular to that plane. The presence of a particular structure in which weak ferromagnetism is possible, and a particular plane in which the magnetic moments may be noncollinear, is related, as shown in Chap. V, to the fact that the magnetic atoms in positions of the c type lie on a mirror symmetry plane σ_y , which is parallel to the XZ plane. A weakly ferromagnetic structure (corresponding to the first and second rows of Table 7) and a noncollinear antiferromagnetic structure (corresponding to the fifth and sixth rows of Table 7) are shown in Fig. 23c and 23d. The latter structure will be called a "cross" structure.

We shall now consider the fourfold position b of the D_{2h}^{17} group (cf. Fig. 7b and the discussion in Sec. 2 of Chap. V). Since this position is located on the mirror plane σ_x , noncollinear structures are possible in this case; these structures are similar to the c -position case of the group D_{2h}^{16} . The only difference is that now noncollinear structures are formed in a plane perpendicular to the X axis.

We shall assume again that the chemical and magnetic unit cells are identical and we shall use the numbering of the magnetic moments of sublattices which was employed for basal lattice sites (Sec. 2, Chap. V), i.e.,

$$M_1 (0 \ 1/2 \ 0), \quad M_2 (1/2 \ 0 \ 0), \quad M_3 (1/2 \ 0 \ 1/2) \quad \text{and} \quad M_4 (0 \ 1/2 \ 1/2).$$

As independent symmetry elements, we shall take the mirror planes σ_z and σ_x , an inversion center I , and a translation $T [1/2 \ 1/2 \ 0]$. Thus the initial collinear structures F and A_i (using the same definition of the vectors L_i as in Table 6) correspond to the following combinations of parities with respect to the four listed symmetry elements (σ_z, σ_x, I, T):

$$F (+ + + +), A_1 (- + + -), A_2 (+ + + -), A_3 (- + + +)$$

and because the structure is always even with respect to σ_x and I , it is sufficient to indicate the parity with respect to σ_z and T .

It is then easy to deduce the third column of Table 7 which unifies in a single row the components of the vectors M and L_i which are transformed in the same way. Thus, the possible magnetic states for the b positions of the D_{2h}^{17} group may be obtained from the analogous states for the c positions of the D_{2h}^{16} group by the following transformation of coordinates $(XYZ) \rightarrow (ZXY)$.

2. INFLUENCE OF THE NONCOLLINEARITY OF MAGNETIC MOMENTS ON THE PROPERTIES OF AN ANTIFERROMAGNET

We shall now determine the role of the noncollinearity of sublattice magnetic moments in an antiferromagnet using the simplest "cross" structure shown in Fig. 23d. An important consequence of the noncollinearity of magnetic moments is the appearance of a nonzero longitudinal magnetic susceptibility χ_{\parallel} at absolute zero.* In order to establish which parameters govern the quantity χ_{\parallel} , we shall calculate it below.

It is desirable to consider the positions b of the D_{2h}^{17} group because the results will be needed later. According to the third column in Table 7 the energy of the system in this case is

$$\begin{aligned} \frac{\mathcal{H}_0}{V} = & \frac{A_0}{2} m^2 + \frac{a_y}{2} m_y^2 + \frac{a_z}{2} m_z^2 + \frac{B_1}{2} l_1^2 + \frac{B_2}{2} l_2^2 + \frac{B_3}{2} l_3^2 + \\ & + \frac{b_{1y}}{2} l_{1y}^2 + \frac{b_{1z}}{2} l_{1z}^2 + \frac{b_{2y}}{2} l_{2y}^2 + \frac{b_{2z}}{2} l_{2z}^2 + \frac{b_{3y}}{2} l_{3y}^2 + \frac{b_{3z}}{2} l_{3z}^2 + \\ & + d_1 m_y l_{3z} + d_2 m_z l_{3y} + w_1 l_{1y} l_{2z} + w_2 l_{1z} l_{2y} - mh, \end{aligned} \quad (10.2)$$

where $m = M/M_0$, $l_i = L_i/M_0$, $h = M_0 H$ and $M_0/4$ is the maximum magnetization of each of the sublattices.

Let us now assume that the relationship between the exchange parameters A and B_i is such that the corresponding exchange forces give rise to the antiferromagnetic structure A_1 . The principal antiferromagnetic vector is then the vector L_1 , and the appearance of other vectors is due to the presence of Dzyaloshinskiy terms in the energy (terms with the coefficients d and w).

The determination of the minimum of (10.2) at $H = 0$ indicates that the "cross" structure in the YZ plane with $L_1 > L_2$ and $L_3 = 0$ does indeed represent one of the possible states (Fig. 24, continuous lines). The equilibrium angle 2α between the vectors

*Since the system is represented by two antiferromagnetic vectors L_1 and L_2 , the longitudinal susceptibility will be understood to be the susceptibility along the direction of the largest vector (in our case, L_1), which is called the principal antiferromagnetic vector.

is determined by the relationship

$$\tan 2\alpha = \frac{2w_1}{B_2 - B_1 + b_{2z} - b_{1y}}. \quad (10.3)$$

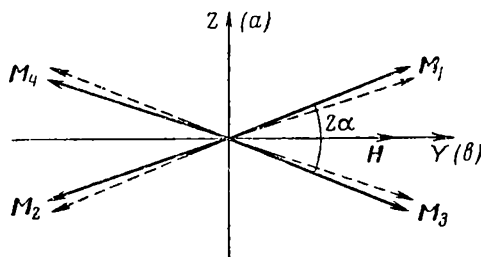


Fig. 24

Let us now apply an external field H along the direction of the principal antiferromagnetic vector (the Y axis). This field will reduce the angle between the vectors M_1 and M_3 and increase the angle between the vectors M_2 and M_4 so that a resultant magnetization will appear along the field direction. This magnetization can be easily found by minimizing the energy (10.2) for $H = H_y$.*

To within terms not higher than the first order in H , we have

$$m_H = h \frac{\tan^2 \alpha}{B_3 - B_1 + b_{3z} - b_{1y} + (A - B_2 + a_y - b_{2z}) \operatorname{tg}^2 \alpha + 2(d_1 - w_1) \tan \alpha}, \quad (10.4)$$

where the angle α is defined by (10.3).

For small values of α [when the right-hand part of (10.3) is small compared with unity], instead of (10.4) we obtain approximately

$$m_H = \frac{h}{B_3 - B_1} \left(\frac{w_1}{B_2 - B_1} \right)^2.$$

Consequently, the required longitudinal susceptibility is, in our approximation:

$$\chi_{\parallel} = \frac{M_0^2}{B_3 - B_1} \left(\frac{w_1}{B_2 - B_1} \right)^2. \quad (10.5)$$

*Here, we are assuming that $M_i^2 = \text{const}$, thus automatically neglecting the possible g -tensor anisotropy. This anisotropy may be allowed for in exactly the same way as in Sec. 4 of Chap. V in the case of two magnetic sublattices. The magnetic moments M_i and the angular momentum I_i , have, in general, different directions (so that the angle α of the cross formed by the magnetic moments is somewhat different from the corresponding angle for the cross formed by the angular momentum).

For comparison, we shall give, in the same approximation, an expression for the transverse susceptibility (i.e., the susceptibility along the axes X and Z):

$$\chi_{\perp} = \frac{M_0^2}{A_0 - B_1}.$$

Thus, when the noncollinearity of magnetic moments, which is given qualitatively by the ratio

$$\frac{\omega_1}{B_2 - B_1}, \quad (10.6)$$

is small, the susceptibility χ_{\parallel} at $T = 0^\circ\text{K}$ is small compared with χ_{\perp} and the value of latter itself remains, in the first approximation, the same as in the case of collinear structures (because $A_0 - B_1 \equiv A$). This is one of the conditions which has allowed us to consider weakly ferromagnetic structures by means of the two-sublattice representation.

The calculation of the spectrum free oscillations of the magnetizations M_j using the Hamiltonian (10.2) indicates that a weak perturbation of the parallelism of the sublattice magnetic moments (by forces of magnetic origin) has little effect on the spin-wave energy of an antiferromagnet and, consequently, on its resonance and thermodynamic properties.*

Nevertheless, in some cases when the ratio (10.6) is sufficiently large, the noncollinearity of the magnetic moments in a compensated antiferromagnet may affect quite strongly the properties of the latter: it may affect χ_{\parallel} and χ_{\perp} , the relationship between their temperature dependences and the resonance frequencies. A calculation carried out by Naish [135] indicates, in particular, that if the noncollinearity of magnetic moments is neglected in dealing with the resonance properties, an error may be introduced into the determination of the g factor of an antiferromagnet.

All these considerations of the role of the noncollinearity of the magnetic moments of sublattices of the "cross" structure apply, at least qualitatively, to noncoplanar structures, both antiferromagnetic (Fig. 23b) and weakly ferromagnetic (Fig. 23a). In the latter case, $\chi_{\parallel} \neq 0$ at $T = 0^\circ\text{K}$ because of the presence of a spontaneous moment (cf. Sec. 1 of Chap. VIII).

*The number of spin-wave modes is now not two but four, in accordance with the number of magnetic sublattices. However, two of these modes have energy gaps governed by an exchange interaction and the other two have gaps governed by the geometric mean values of the exchange and magnetic anisotropy energies. The latter two modes can in fact be reduced, by introducing some "effective" parameters, to the oscillation modes of an antiferromagnet with two sublattices. As far as the first two (additional) modes are concerned, they do not affect the properties of the system in the case of a weak perturbation because of their high activation energy.

Examples of antiferromagnets with a noncollinear magnetic structure are the anhydrous copper and cobalt sulfates (CuSO_4 and CoSO_4), investigated by Borovik-Romanov and Kreines [136, 137, 97].

The Néel point of CuSO_4 is 34.5°K and its symmetry group is D_{2h}^{16} , with the Cu^{++} ions in the b position [138]. Consequently, in an antiferromagnetic state, CuSO_4 should have a noncoplanar structure of the type shown in Fig. 23b. It is possible that the finite value of the longitudinal susceptibility at $T \rightarrow 0^\circ\text{K}$ is related to the noncollinearity of the magnetic moments and is not due to inaccurate alignment of the sample, as suggested by Kreines [136].

The symmetry group of CoSO_4 crystals is D_{2h}^{17} with the Co^{++} ions in the b position [139]. Below the Néel point ($\Theta_N \approx 12^\circ\text{K}$), the susceptibilities along orthorhombic axes, selected in such a way that $a > b > c$, satisfy the following relationship:

$$\chi_b > \chi_c > \chi_a. \quad (10.7)$$

This leads us to suggest that the magnetic structure of cobalt sulfate is the "cross" structure oriented along the orthorhombic a axis (i.e. the principal antiferromagnetic vector is directed along this axis).

We shall now consider another important property of CoSO_4 crystals. If they are magnetized along the c axis, the magnetic moment increases linearly with the field up to 12 kilooersteds. On further increase in the field, the magnetization at low temperatures (4.2°K) rises very rapidly, increasing by a factor of almost 20 for a 1 kilooersted change in the field, and this is followed by a weak rise (Fig. 25). The maximum magnetic moment obtained in a field $H = 18$ kilooersteds is approximately 6,000 cgs emu/mole. This is only 30% of the nominal moment (i.e., the moment calculated on the assumption that all the magnetic moments of the Co^{++} ions are strictly parallel). Therefore, the phenomenon shown in Fig. 25 is a field-induced transition to a weakly ferromagnetic structure (corresponding to rows 1 and 2 in Table 7), which is due to the superposition of the structures A_3 and F (Kreines [97]). The energy given by (10.2) includes terms (with d_1 and d_2) which, on the appearance of field-induced magnetization along the Y or Z axis, also give rise to $L_3 \neq 0$, so that the initial structure A_1 (with an admixture of A_2) acquires an admixture of A_3 . In a sufficiently strong field, capable of overcoming the difference between the energies of the initial structure and the field-induced structure A_3 (with an admixture of F), the latter structure becomes energetically more favored and consequently the transition described above takes place.*

*The presence in the magnetic-energy expression of mixed terms of the $M_\alpha L_{i\beta}$ type may lead to field-induced antiferromagnetic ordering even in the paramagnetic region

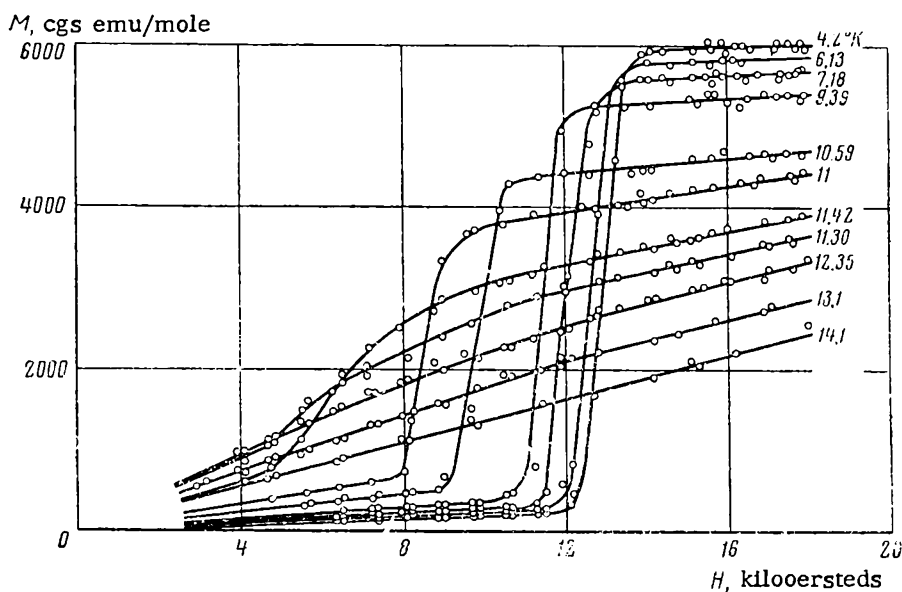


Fig. 25

Summarizing our discussion, we may conclude that anhydrous cobalt sulfate has the antiferromagnetic structure $A_1 + A_2$, for which the magnetic moments M_1 and M_3 , antiparallel to M_2 and M_4 , respectively, lie in planes perpendicular to the orthorhombic axis b (X axis in our notation, Fig. 24). In strong fields along the c direction (Z axis in our notation), there is a transition to the structure $A_3 + F$, for which the magnetic moments of the sublattices lie in the same planes, and $M_1 \parallel M_2$ and $M_3 \parallel M_4$ (cf. Fig. 23c after the substitution of $XYZ \rightarrow ZXY$). It would be desirable to check these conclusions by direct neutron diffraction studies of the magnetic structure of CoSO_4 .

In conclusion, we note that in the case of rare-earth orthoferrites with weak ferromagnetism, considered in Chap. VIII (in particular, HoFeO_3 and ErFeO_3), neutron diffraction investigations of the magnetic structure [122] showed several weak diffraction peaks which could not be accounted for by assuming that the magnetic moments of the sublattices were parallel in pairs. It is possible that these peaks are related to the presence of non-collinearities of the type discussed above (noncoplanar structures and "crosses").

[93]. Then the vector L_i , in its turn, increases M , and therefore, the observed effect may explain the very sharp magnetic susceptibility peak near the Néel point observed in some antiferromagnetic crystals (in which weak ferromagnetism is possible) along the directions which permit a weak ferromagnetic moment. Such a susceptibility peak (along the a -axis direction) is observed also for CoSO_4 , which is one more argument favoring the hypothesis put forward by Kreines [97] on the nature of this transition in cobalt sulfate.

CHAPTER XI

Ferromagnetism and Antiferromagnetism in a System of Two Crystallographically Nonequivalent Magnetic Sublattices

So far, we have considered magnetic structures consisting of one system of crystallographically equivalent magnetic atoms (or ions). Such structures, if they are collinear or slightly noncollinear, may be described by two equivalent magnetic sublattices. To consider the role of the crystallographic nonequivalence of the magnetic atoms, we shall deal with the simplest case of a system consisting of two nonequivalent magnetic sublattices in the sense that no symmetry operation can bring the sites of one sublattice into coincidence with sites in the other. We shall also consider another variant of ferromagnetism due, first, to numerical differences between the g factors of nonequivalent sublattices, and secondly, to a different temperature dependence of their magnetic moments.

1. FERRIMAGNETISM

In order to establish the principal features connected with the crystallographic nonequivalence of magnetic sublattices, we shall consider just the isotropic case, including only the exchange interaction terms of all the internal interactions. The energy density given by (1.2) then becomes

$$\mathcal{H}(\mathbf{r}) = B_{12}(\mathbf{m}_1 \mathbf{m}_2) + \frac{1}{2} C_{jj'} (\nabla m_{j\alpha} \nabla m_{j'\alpha}) - (\mathbf{M}_1 + \mathbf{M}_2) \mathbf{H}. \quad (11.1)$$

It is easily seen that the minimum of this energy corresponds to a uniform and antiparallel distribution of the magnetizations

M_1 and M_2 , oriented along and against the direction of the field H , if the following conditions are satisfied

$$B_{12} > 0 \text{ and } H < (M_{10} - M_{20}) B_{12}.$$

Here, M_{10} and M_{20} are the maximum values of the projection of the magnetizations of the first and second sublattices (we are assuming that $M_{10} > M_{20}$). The resultant magnetization along the H direction is $M_{10} - M_{20}$.

The free oscillations of the magnetizations M_1 and M_2 near the ground state may be found by solving the classical equations of motion (1.8) or by a quantum-mechanical method (Chap. I, Sec. 2). This calculation yields the following energy values for the two spin-wave modes:

$$\varepsilon_k^{(1,2)} = \sqrt{\left(\frac{\alpha_1 - \alpha_2}{2}\right)^2 + \alpha_1 \alpha_2 - \beta^2} \pm \frac{\alpha_1 - \alpha_2}{2}, \quad (11.2)$$

where

$$\begin{aligned} \alpha_1 &= \frac{\mu_1}{M_{10}} (B_{12} + C_{11}k^2) + \mu_1 H, \\ \alpha_2 &= \frac{\mu_2}{M_{20}} (B_{12} + C_{22}k^2) - \mu_2 H, \\ \beta &= \left(\frac{\mu_1 \mu_2}{M_{10} M_{20}}\right)^{1/2} (B_{12} + C_{12}k^2). \end{aligned}$$

If the resultant angular momentum of the system (the mechanical moment)

$$S_0 = \frac{M_{10}}{\mu_1} - \frac{M_{20}}{\mu_2} \quad (11.3)$$

is not zero, we are dealing with ferrimagnetism. In this case, bearing in mind that the first terms (i.e., the terms with B_{12}) in α_1 , α_2 and β are the largest, so that $(\alpha_1 - \alpha_2)^2 \gg |\alpha_1 \alpha_2 - \beta^2|$, the spin-wave energies (11.2) may be represented in the following approximate form:

$$\varepsilon_{1k} = \frac{\alpha_1 \alpha_2 - \beta^2}{|\alpha_1 - \alpha_2|}, \quad \varepsilon_{2k} = |\alpha_1 - \alpha_2| + \frac{\alpha_1 \alpha_2 - \beta^2}{|\alpha_1 - \alpha_2|}. \quad (11.4)$$

If we restrict ourselves to the first terms in the expansion of $\varepsilon_k^{(1,2)}$ in k , we have

$$\varepsilon_{1k} = I_1 k^2 + \mu_{\text{eff}} H, \quad (11.5)$$

$$\varepsilon_{2k} = \left| \frac{\mu_2}{M_{20}} - \frac{\mu_1}{M_{10}} \right| B_{12} + I_2 k^2 - \frac{1}{2} (\mu_1 + \mu_2) H, \quad (11.6)$$

where I_1 and I_2 are certain combinations of the constants C_{11} , C_{22} , and C_{12} , for example,

$$I_1 = \frac{\mu_{\text{eff}}}{M_{10} - M_{20}} (C_{11} + C_{22} - 2C_{12}); \quad (11.7)$$

μ_{eff} is the effective value of the spectroscopic splitting factor (multiplied by the Bohr magneton), given by the ratio of the resultant magnetic moment of the system to the resultant angular momentum, i.e.,

$$\mu_{\text{eff}} = \frac{M_{10} - M_{20}}{S_0}.$$

Thus, the energy of the first spin-wave mode (11.5) is completely analogous to the corresponding expression (2.23) for normal ferromagnets, except that the constants representing a substance (I and μ) are replaced in ferrimagnets by their effective values given by (11.7) and (11.8). The second mode is altogether absent in normal ferromagnets, while in ferrimagnets it appears on the introduction of two sublattices, which are necessary to describe ferrimagnetism.

The first mode has an energy gap

$$\varepsilon_{10} = \mu_{\text{eff}} H, \quad (11.9)$$

which is due to the energy in the external magnetic field and which vanishes when $H = 0$. Using the terminology introduced in Chap. I (Sec. 2), we shall call this mode "acoustical." The second oscillation mode (as expected, $S_0 \neq 0$) is "optical" since its activation energy is

$$\varepsilon_{20} \simeq \left| \frac{\mu_2}{M_{20}} - \frac{\mu_1}{M_{10}} \right| B_{12}, \quad (11.10)$$

which is determined by the exchange interaction between the sublattices and amounts to 10^{-14} – 10^{-13} erg per magnon. The corresponding resonance frequency, sometimes called the exchange resonance frequency, should be in the infrared region and therefore cannot be detected by magnetic radiospectroscopy methods.*

This example shows once again that the properties of a ferromagnet under relatively "weak" external perturbations, whose

*This does not apply to temperatures near the compensation point of ferrites which have such a point.

energies are small compared with the exchange energy, are completely determined solely by the "acoustical" oscillation mode. Therefore, all the results obtained in Chaps. II and III for a normal ferromagnet may be applied also to ferrimagnets.

2. LONGITUDINAL WEAK FERROMAGNETISM AND THERMAL FERROMAGNETISM

We shall now consider the case of spin antiferromagnetism for which $S_0 = 0$. In this case, at absolute zero there is complete compensation of the angular momenta of the sublattices, given by the equality

$$\frac{M_{10}}{\mu_1} = \frac{M_{20}}{\mu_2} \quad (11.11)$$

when the resultant magnetic moment is not equal to zero because of the numerical differences between the g factors of this sublattice.* This spontaneous magnetic moment is directed along the antiferromagnetic axis ("longitudinal weak ferromagnetism") and is given by

$$M_s(0) = M_{10} - M_{20} = \frac{\Delta\mu}{\mu} M_0, \quad (11.12)$$

where

$$\Delta\mu = \frac{\mu_1 - \mu_2}{2}, \quad \mu = \frac{\mu_1 + \mu_2}{2}.$$

We shall now calculate the total magnetization of such a system as a function of temperature and field. From a relationship of the (2.27) type, taking into account the two spin-wave modes (11.5) and (11.6) and the condition (11.11), we find

$$M_H(T) = M_s^I(T) + M_s^{II}(T) + \chi_{\parallel} H, \quad (11.13)$$

where

$$M_s^I(T) = M_s(0) \left(1 - \frac{4\chi_{\parallel} H_E}{M_0} \right) \quad (11.14)$$

and

$$M_s^{II}(T) = \frac{2\pi^2\mu}{15} \frac{I^*}{I} \left(\frac{\kappa T}{I} \right)^4. \quad (11.15)$$

*For simplicity, we shall assume that the g factors are isotropic.

In the above formulas χ_{\parallel} is the usual longitudinal susceptibility of an antiferromagnet, the temperature dependence of which is given, for example, by the formula (4.60) ($\chi_{\parallel} \sim T^2$);

$$I = \frac{\mu}{M_0} \sqrt{B_{12}(C_{11} + C_{22} - 2C_{12})}, \quad I^* = \frac{\mu}{M_0} (C_{11} - C_{22}).$$

Thus, according to (11.13), the spontaneous magnetization of our system of two nonequivalent magnetic sublattices consists of two parts at $T \neq 0^\circ\text{K}$. One of them is the usual longitudinal weak ferromagnetism, due to the difference between the g factors of the sublattices. This part of the magnetization is identical, except for the sign, with the spontaneous magnetization given by (7.51) for the longitudinal weak ferromagnetism due to the g factor anisotropy in a system of equivalent magnetic sublattices (the difference being that instead of $\tau = g_{xy}/g_{\perp}$, we have here the quantity $\Delta\mu/\mu$). The second part of the spontaneous magnetization is due to the difference between the exchange interaction parameters of the first (C_{11}) and second (C_{22}) sublattices. It appears only at $T \neq 0^\circ\text{K}$ due to the different temperature dependences of the angular momenta of the sublattices, so that the compensation observed at $T = 0^\circ\text{K}$ no longer applies. The appearance of M_s^{II} is not due to the difference between the g factors but is due to exchange forces. Therefore, at sufficiently high temperatures, this part of the magnetization may, in general, be of the same order of magnitude as M_0 (if $I^* \sim I$). We shall call the appearance of the spontaneous magnetization at $T \neq 0^\circ\text{K}$ the "thermal ferromagnetism."*

The quantities M_s^{I} and M_s^{II} may have the same (when $C_{11} > C_{22}$) or opposite (when $C_{11} < C_{22}$) signs. In the latter case, the total spontaneous magnetization should pass through zero at some temperature between absolute zero and the Curie point. In other words, there should be a compensation point where the longitudinal weak ferromagnetism is compensated by the thermal ferromagnetism. It is possible that this was what Aléonard and Pauthenet observed (private communication) in $\text{NbO}_5 \cdot 4\text{NiO}$ (nickel niobate) [141].

*The calculation carried out above is, as far as the author knows, the first derivation of the temperature dependence ($M_s \sim T^4$) in the low-temperature part of the L -type [40] $M_s(T)$ curve.

Conclusions

The present monograph advances a unified theory of a wide range of mutually related phenomena, based on certain general modern concepts of the nature of the magnetically ordered state of matter and the symmetry properties of crystals. In contrast to some earlier theories which used a special selection of parameters to describe a particular phenomenon, we have attempted to establish connections between the various effects using qualitative or quantitative relationships which are, where possible, independent of any parameters. Such relationships are of the greatest value from the point of view of verifying experimentally the initial theoretical assumptions. Therefore, in the conclusions about to be drawn we shall concentrate particularly on these relationships. The order of presentation of the conclusions is not related to their importance but follows, in the main, the plan of the book.

|

Ferromagnetism is the magnetically ordered state of matter which has been investigated most thoroughly, both theoretically and experimentally. Therefore, we shall consider here the effects which are "fine" and complex, and have hitherto been regarded as secondary. Further experimental studies of ferromagnets should include measurements of the saturation magnetization as a function of temperature and field for the purpose of obtaining information on the phenomena related to the intrinsic magnetization at low temperatures (Sec. 2, Chap. II). Measurement of the intrinsic magnetization, which is given by the second term in (2.35)

$$M_i \simeq 0.08 \mu \frac{\kappa T}{I} \left(\frac{uH}{I} \right)^{1/2},$$

provides a further opportunity of determining independently the exchange coupling parameter I , additional to that based on the

measurement of the spontaneous magnetization, the spin contribution to the specific heat or the spin-wave resonance in films. Moreover, we can check indirectly whether the allowance for the influence of an external magnetic field on the spin system is made correctly in the spin-wave theory.

Measurements should be carried out on single-crystal samples magnetized along the easy axis.

II

It would be interesting also to investigate in detail the temperature dependence of the magnetization curves of uniaxial ferromagnets along the hard direction; we mean here only those parts of the curves which represent the rotation processes (Sec. 3, Chap. II). A check of the temperature dependence of the magnetic susceptibility for these processes

$$\chi_{\text{rot}} = \frac{M_H}{H} = \chi_{\text{rot}}(0) (1 + \text{const} \cdot T^{3/2}) = \chi_{\text{rot}}(0) \frac{M_s(0)}{M_s(T)} \quad (\text{I})$$

is desirable also because this susceptibility is in some respects an analog of the transverse magnetic susceptibility of antiferromagnets (the intrinsic susceptibility along the easy direction is the analog of the longitudinal susceptibility of an antiferromagnet). Starting from ferromagnets, it should be possible to find the reasons for the disagreement between theory and experiment in the case of the transverse susceptibility of antiferromagnets (see Conclusion VI). Measurements are best carried out on uniaxial single-crystal ferromagnets with their easy axis in the basal plane and the magnetization along the principal axis of the crystal.

It is also important to measure the temperature dependence of the magnetic susceptibility χ_{rot} along the hexagonal axis (which is the hard axis) of ferromagnetic dysprosium at temperatures $\kappa T \ll \mu H_a$ (Sec. 4, Chap. II). According to (2.56), in this case we have, in contrast to equation (I),

$$\chi_{\text{rot}} = \chi_{\text{rot}}(0) (1 + \text{const} \cdot T^4).$$

III

Systematic investigations are needed of the temperature dependence of the magnetocrystalline anisotropy constants and magnetostriction constants of ferromagnets at low temperatures (Chap. III). The establishment of relationships governing the

deviation from the general theoretical formula for the anisotropy constants

$$\frac{K_N(0) - K_N(T)}{K_N(0)} = N(2N + 1) \frac{M(0) - M(T)}{M(0)}$$

and the verification of a similar formula (3.36) for the magnetostriction constants is necessary for the further development of our ideas on the nature of magnetic phenomena represented by the behavior of a ferromagnet in external fields (the "technical" magnetization curve, ferromagnetic resonance, etc.).

It is necessary to carry out a correct harmonic analysis (expansion in harmonic polynomials) to interpret the experimental data for the magnetocrystalline anisotropy energy and magnetoelastic energy.

Investigations of the nature of the forces responsible for the magnetic ordering would be helped by measurements of the volume magnetostriction (thermostriction and intrinsic magnetostriction) and, in particular, by the verification of the relationships given in (3.42).

IV

In the case of antiferromagnetic crystals, it is necessary to establish first of all how well the parameters characterizing the antiferromagnetic state (for example A , a , and b , for uniaxial crystals) obtained from static measurements (magnetic susceptibility and its anisotropy) and from antiferromagnetic resonance (Secs. 2 and 3 of Chap. IV) agree with one another. We shall now quote examples of possible comparisons:

a) The characteristic field $H_{\parallel} = \sqrt{(A + |b|)|b|} / M_0 = \sqrt{|b|/\chi_{\perp}^y}$, which gives the limit of stability of the state in which the antiferromagnetic axis ($\mathbf{l} \parallel \mathbf{H} \parallel \mathbf{Z}$) is parallel to the field $\mathbf{H} = H_z$, can be determined both from the magnetization curves (Fig. 6a or 6b) and from the resonance frequencies (4.29) or (4.37) by extrapolation to $H = 0$.

b) From formulas (4.12), (4.19), and (4.20), the following relationship can be deduced:

$$\frac{H_{\perp} - H_{\parallel}}{H_{\parallel}} = \frac{1}{\chi_{\perp}^y} \left(\frac{1}{\chi_{\perp}^z} - \frac{1}{\chi_{\perp}^y} \right),$$

this gives the relative width of the transition region between the states $\mathbf{l} \parallel \mathbf{H} \parallel \mathbf{Z}$ and $\mathbf{l} \perp \mathbf{H} \parallel \mathbf{Z}$ in terms of the two transverse susceptibilities of a uniaxial antiferromagnet with its spontaneous antiferromagnetic axis parallel to the principal crystal axis. On

the other hand, H_{\parallel} and H_{\perp} may be determined separately from the resonance frequency ω_1 (4.37) for the state $\mathbf{l} \parallel \mathbf{Z}$, $\mathbf{H} \perp \mathbf{Z}$, because in this case

$$H_{\parallel}^2 + H^2 \frac{H_{\perp}}{H_{\parallel}} = \left(\frac{\omega_1}{\gamma} \right)^2$$

(the gyromagnetic ratio γ may be found from the resonance frequencies of another state, for example, $\mathbf{l} \parallel \mathbf{H} \parallel \mathbf{Z}$).

c) Similarly an analogous relationship between the transverse susceptibilities of (4.23) (along and at right angles to the crystal axis) and the resonance frequency ω_1 given by (4.43) may be established for an antiferromagnet with its antiferromagnetic axis in the basal plane. Then, according to (4.40), we obtain

$$\frac{\chi_{\parallel}^x}{\chi_{\perp}^z} = \left(\frac{\omega_1}{\gamma H} \right)^2.$$

V

There is great interest in the theoretically predicted nonlinear effect of the longitudinal magnetization of an antiferromagnet by a transverse circularly polarized field under antiferromagnetic resonance conditions (Sec. 3, Chap. IV). The experimental difficulties reduce to a search for an antiferromagnet with a sufficiently narrow resonance line.

VI

An experimental study of the temperature dependence of the transverse magnetic susceptibility (Sec. 4, Chap. IV) is the most important problem relating to the thermodynamic properties of antiferromagnets.

This applies particularly to those antiferromagnets for which the theory gives the quadratic temperature dependence

$$\Delta \chi_{\perp} = - \frac{1}{4} \alpha T^2 \quad (\text{II})$$

in a sufficiently wide range of temperatures. Among these are uniaxial crystals with the antiferromagnetic axis in the basal plane (the x/\perp , state, cases "a" and "b" of Sec. 4, Chap. IV) as well as other antiferromagnets for which $\mu H_{EA} \ll \kappa \Theta_N$.

If the relationship (II) is not satisfied, it would be desirable to establish whether any definite relationships apply to the dependence $\chi_{\perp}(T)$ by investigating various antiferromagnets having different magnetocrystalline structures and different atomic spins S .

The cases for which the theory predicts that $\Delta\chi_{\perp}$ should be proportional to T^4 [for example, formula (4.76)] are also worth investigating.

Other relationships governing the temperature dependence of the magnetic susceptibility and spin specific heat which require experimental verification [for example, (4.83) relating χ_{\parallel} and C_s] are discussed in greater detail in the conclusions of Sec. 4, Chap. IV, and therefore we shall not consider them here.

VII

The investigation of weak ferromagnetism in antiferromagnets is of special interest in the theory of ferromagnetism and antiferromagnetism. This is because a weak ferromagnetic moment is a directly observable quantity, due to magnetic (relativistic) forces, and appears only in the first approximation on a "zeroth order" background, while similar effects in ferromagnets give rise only to correction terms. Therefore, the theoretical models scarcely reflect the calculated properties of ferromagnets and normal antiferromagnets (such as the constancy and isotropy of the moduli of the local magnetic moments or angular momentum, the isotropy or anisotropy of gyromagnetic tensors, etc.), but are directly reflected in the phenomenon of weak ferromagnetism itself, modifying its various characteristics. Moreover, the presence in the thermodynamic potential of weak ferromagnets of mixed terms of the $m_{\alpha}l_{\beta}$ type, which relate the magnetic vector m and the antiferromagnetic vector l , make it possible to fix the sign of the vector l by an external field and, consequently, to assign at will the magnetic moments of a given direction to given crystal lattice sites. This is of great importance in solving the problem of the limits of applicability and the meaning of the concept of magnetic sublattices, the "lifetime" of these sublattices, etc.

VIII

The condition of parity of an antiferromagnetic structure with respect to translations and an inversion center (Sec. 1, Chap. V) makes it possible to find easily all structures exhibiting weak ferromagnetism (we are speaking here of collinear and slightly noncollinear magnetic structures). Weak ferromagnetism should exist in all antiferromagnetic structures for which translations and inversion centers of the chemical lattice are also translations and inversion centers of the magnetic lattice. This means, in particular, that for weak ferromagnetism to exist, a unit cell must contain not less than two magnetic atoms unrelated by an inversion center (or translations if the unit cell is not primitive).

Weak ferromagnetism should be absent in cubic crystals of T and T_n symmetry classes.

In considering only collinear and slightly noncollinear structures (with the noncollinearity due to magnetic forces), one restricts greatly the generality of the conclusions; but there is a positive aspect: the appearance of weak ferromagnetism when the parity condition is not obeyed is an unambiguous indication of a considerable noncollinearity of the magnetic moments, the noncollinearity now being of exchange origin.

A more general theoretical classification of weakly ferromagnetic structures, given in Table 3, includes also collinear and slightly noncollinear structures.

IX

It follows from Table 3 that all the weakly ferromagnetic structures considered here can be divided according to their properties into five types:

1. The structures of all uniaxial crystals, even with respect to the principal symmetry axis (i.e., structures in which the atoms related by this axis have magnetic moments directed in the same way).

2. The structures of tetragonal crystals, odd with respect to a fourfold symmetry axis (this axis brings into coincidence the sites with antiparallel collinear magnetic moments).

3. The structures of cubic and hexagonal crystals, odd with respect to fourfold and sixfold symmetry axes, respectively, in which only higher-order weak ferromagnetism may exist.

4. The weakly ferromagnetic structures of orthorhombic crystals.

5. The weakly ferromagnetic structures of monoclinic crystals.

X

The characteristic features of type I structures, which have been studied theoretically and experimentally more extensively than the others, are as follows (Chap. VI):

- a) the isotropy of the weak ferromagnetic moment M_s (in the first approximation) with respect to rotation in the basal plane and the transverse nature of weak ferromagnetism ($M_s \perp l$ always);

- b) the monotonic decrease of the spontaneous magnetization with increase of temperature in accordance with the law $M_s(T) = M_s(0)(1 - \eta T^2)$, where the coefficient η increases by a factor of 2 on transition from the temperature region $\varepsilon_{20} \gg \kappa T$ to the temperature range $\kappa \Theta_N \gg \kappa T \gg \varepsilon_{20}$;

c) the usually weak anisotropy of the resonance frequency which depends on the direction of the external field in the basal plane;

d) the possibility of describing weakly ferromagnetic phenomena by means of one parameter ($\bar{d} = d + \tau A$) and the related indistinguishability of the two mechanisms of the origin of weak ferromagnetism (noncollinearity of the angular momenta, due to magnetocrystalline anisotropy forces, or asymmetric components of the gyromagnetic tensor).

It would be desirable to carry out the following experimental studies on weak ferromagnets of this type:

1) investigate the initial (nonlinear part of the magnetization curve (until it reaches the straight line $M_H = M_s + \chi_\perp H$, Fig. 14) and the residual magnetization of MnCO_3 and $\alpha\text{-Fe}_2\text{O}_3$ as a function of the sample's history (its chemical purity and the perfection of its lattice, effect of thermomagnetic treatment, etc.) in order to find the reason for the wide range of fields ($\sim 10^3$ oersteds) in which the curve is nonlinear; the theoretically expected value is $\leq 10^2$ oersteds;

2) check carefully whether the relationship (6.17) between the temperature dependences of the spontaneous magnetization and the spin specific heat is satisfied.

XI

From the theoretical point of view, the most interesting objects of experimental study are weakly ferromagnetic structures of type II (for example, NiF_2). The expected properties of weak ferromagnets of this type, which need experimental verification, are as follows (cf. Secs. 1 and 2 in Chap. VII):

a) the need to introduce two parameters to describe weak ferromagnetism: the coefficient d of the corresponding invariant in the Hamiltonian and the parameter $\tau = g_{xy}/g_\perp$ or $(g_{xx} - g_{yy})/g_{xx}$ for the structures $4_z^- 2_d^+$ or $4_z^- 2_d^-$ respectively;

b) the possibility of transverse and longitudinal magnetism (states of type II_1 and II_2);

c) the strong anisotropy of the "spontaneous" magnetic moment, found by extrapolating the magnetization curve to $H = 0$ from the strong-field region [formulas (7.31) and (7.36), Fig. 18] if the model assumption (5.10) is made about the angular momenta of the sublattices; in the thermodynamic theory of Dzyaloshinskiy [14], where instead of (5.10) a more plausible condition ($I^2 = \text{const}$) is used, there should be no anisotropy of this type and, therefore, the experiment should determine the applicability of one or the other model;

d) the specific nature of the magnetization curves along and opposite the direction of spontaneous magnetization, and at right angles to this magnetization for various special cases (Figs. 15-17);

e) the singularities of the temperature dependence of the spontaneous magnetization [formulas (7.41) and (7.42)]: the possibility of a monotonically decreasing curve $M_s = M_s(T)$, as well as a curve with a maximum; the latter should occur when $1 < |A\tau/d| < 5$, if τ and d have opposite signs;

f) the considerable anisotropy of the resonance frequencies which depend on the magnetic field direction in the basal plane.

XII

The search for weak ferromagnetism in hexagonal crystals having antiferromagnetic structures odd with respect to a sixfold axis (structures of type III, described in Sec. 3, Chap. VII) deserves special attention. Antiferromagnets with the nickel-arsenide lattice exemplify such a structure. Their weak ferromagnetic moment ($M_s \sim l_\perp^2 \sin 3\varphi$, where l_\perp is the component of the vector l in the basal plane) should be directed along the hexagonal axis, its magnitude varying periodically and its sign varying with the angle φ which determines the direction of the vector l_\perp in the basal plane. To detect this moment, we may use not only antiferromagnets with a spontaneous antiferromagnetic axis l_s perpendicular to the hexagonal axis Z , but also crystals with $l_s \parallel Z$ if it is possible to record the magnetization curves in fields above the threshold value ($H > H_t \sim H_{EA}$). As in the case of type I structures, the spontaneous magnetization should decrease monotonically with temperature except that the ratio of the coefficients of T^2 in the temperature ranges $\kappa T \ll \varepsilon_{20}$ and $\kappa T \gg \varepsilon_{20}$ should be not 1/2 but 9/14.

It is possible that in this case weak ferromagnetism could be detected more simply not from static magnetization measurements but by means of antiferromagnetic resonance measurements in which oscillations of frequency ω_1 [formula (9.7)] are excited by a high-frequency field $h_\omega \parallel H \parallel Z$.

XIII

The most characteristic features of weak ferromagnetism in orthorhombic crystals are listed below (cf. also Chap. VIII).

a) The number of specific "weak ferromagnetism" parameters is, in general, four (d_1 , d_2 and τ_1 , τ_2).

b) In weak fields ($H \ll H_{EA}$), the spontaneous magnetic moment appears in practice only along its "spontaneous" direction, while in a plane at right angles to this direction the magnetic properties do not differ greatly from the corresponding properties of a

normal antiferromagnet. In order to check the weak ferromagnetic moment along the other direction permitted by the symmetry, it is necessary to apply along this direction a field which is at least of the order of H_{EA} (i.e., 10^4 – 10^5 oersteds) (cf. Fig. 20).

c) Because of the large number of parameters for orthorhombic crystals, there may be a large number of variants of the temperature dependence of the spontaneous magnetization: apart from a monotonically decreasing curve and a curve with a maximum—mentioned in connection with tetragonal odd structures—we can also have a complex nonmonotonic dependence $M_s(T)$ with a minimum and a maximum (Fig. 21).

d) Both resonance frequencies should, as a rule, lie in the millimeter or far infrared range because the corresponding energy gaps for spin waves are determined by the geometric mean values of the exchange and magnetic anisotropy energies, the latter being quadratic with respect to sublattice magnetizations.

Experimental studies of orthorhombic weak ferromagnets (for example, various orthoferrites) should deal first of all with the magnetization and magnetization-reversal curves of single-crystal samples in sufficiently strong fields above the threshold (i.e., $H > H_{EA}, H'_{EA}$, cf. Fig. 20), as well as with the detailed temperature dependence of the spontaneous magnetization.

It would also be interesting to verify the hypothesis of the noncollinear origin of the spontaneous magnetization of MnP (for details see Sec. 3, of Chap. VIII).

XIV

The properties of monoclinic weak ferromagnets (5 in the foregoing list) have not been considered in the present book. However, it is easily seen that all the main properties just enumerated for orthorhombic crystals are retained, in general, by monoclinic crystals (the number of “weakly ferromagnetic parameters” is even greater).

XV

In the case of noncollinear antiferromagnetic structures (Chap. X), neutron diffraction confirmation of the “cross” structure (Fig. 24), obtained by comparing experiment with theory would be desirable,* as well as a study of the transition to the weakly ferromagnetic state in a magnetic field.

*Recently an article appeared confirming, by neutron diffraction, the “cross” structure [143].

XVI

It would be interesting to find a magnetic substance exhibiting "thermal ferromagnetism" due to different temperature dependences of the magnetic moments of nonequivalent sublattices, mutually compensated at absolute zero (Chap. XI). This is the only case of ferromagnetism (of exchange and not relativistic origin) capable of spin-wave interpretation and for which the temperature dependence of the spontaneous magnetization is affected by both spin-wave modes and $M_s \sim T^4$.

In conclusion, we note that numerous properties of magnetically ordered (collinear and slightly noncollinear) systems may be derived from one very simple semiphenomenological model. A systematic verification of the theoretical conclusions for various types of crystalline magnetic substance, the investigation of various properties (magnetic, static, resonance, thermodynamic, etc.) of the same samples, and the comparison of these properties by means of general relationships predicted theoretically, should make it possible to find and list systematically the main points of divergence between theory and experiment. This, in turn, will suggest ways of further developing the theory.

Appendix A

I. DIAGONALIZATION OF THE QUADRATIC FORM

The general method of diagonalizing the quadratic form of the Bose operators was given by Bogolyubov and Tyablikov [20]. In order to reduce the expression (1.21) to the form from which Bogolyubov and Tyablikov started, we shall introduce the following notation:

$$b_k^j = b_{2j-1}, \quad b_{-k}^j = b_{2j} \quad (j = 1, 2, \dots, n).$$

(1.21) may then be written in the form

$$\mathcal{H}_2(\mathbf{k}) = A_{tt'} b_t^\dagger b_{t'} + \frac{1}{2} B_{tt'} b_t^\dagger b_{t'}^\dagger + \frac{1}{2} B_{tt'}^* b_t b_{t'}, \quad (\text{A.1})$$

where now the summation indices t, t' run from 1 to $2n$, and the coefficients $A_{tt'}$ and $B_{tt'}$, satisfy the conditions

$$\begin{aligned} A_{2j-1, 2j'} = A_{2j, 2j'-1} = 0, \quad A_{2j-1, 2j'-1} = A_{2j, 2j'} = \alpha_{jj'}, \\ B_{2j-1, 2j'-1} = B_{2j, 2j'} = 0, \quad B_{2j, 2j'-1} = B_{2j-1, 2j'} = \beta_{jj'}. \end{aligned} \quad (\text{A.2})$$

According to Bogolyubov and Tyablikov [20], the form (A.1) is made diagonal by a linear transformation of the new Bose operators ξ_t and ξ_t^\dagger :

$$b_t = \sum_s (\xi_s u_{ts} + \xi_s^\dagger v_{ts}^*), \quad b_t^\dagger = \sum_s (\xi_s^\dagger u_{ts}^* + \xi_s v_{ts}). \quad (\text{A.3})$$

$\mathcal{H}_2(\mathbf{k})$ then becomes

$$\mathcal{H}_2(\mathbf{k}) = - \sum_{t,s} E_s |v_{ts}|^2 + \sum_s E_s \xi_s^\dagger \xi_s, \quad (\text{A.4})$$

if the transformation coefficients u_{ts} and v_{ts} are solutions of the system of equations

$$\begin{aligned} \sum_{t'} (A_{tt'} - E\delta_{tt'}) u_{t'} + \sum_{t'} B_{tt'} v_{t'} &= 0, \\ \sum_{t'} B_{tt'} u_{t'} + \sum_{t'} (A_{tt'}^* + E\delta_{tt'}) v_{t'} &= 0. \end{aligned} \quad (\text{A.5})$$

By equating to zero the determinant Δ of this system, we find $2n$ roots for the quantity E (E_1, E_2, \dots, E_{2n}). For each root E_s , we then find the corresponding values of u_t and v_t , i.e., u_{ts} and v_{ts} . The orthogonality and normalization conditions are:

$$\begin{aligned} \sum_t (u_{ts} u_{ts}^* - v_{ts} v_{ts}^*) &= \delta_{ss'}, \quad \sum_t (u_{ts} v_{ts'} - u_{ts'} v_{ts}) = 0, \\ \sum_s (u_{ts} u_{t's}^* - v_{t's} v_{ts}^*) &= \delta_{tt'}, \quad \sum_s (u_{ts} v_{t's}^* - v_{ts}^* u_{t's}) = 0. \end{aligned} \quad (\text{A.6})$$

It is easily shown that, in the present case, if the tensors $A_{tt'}$ and $B_{tt'}$, satisfy the relationships (A.2) and (1.22), the condition for solving the system (A.5) given by $\Delta = 0$ reduces to the form

$$\Delta = \Delta_1^2(E) = \left\| \begin{array}{c|c} \alpha_{jj'} - E\delta_{jj'} & \beta_{jj'} \\ \hline \beta_{jj'}^* & \alpha_{jj'}^* + E\delta_{jj'} \end{array} \right\|^2 = 0. \quad (\text{A.7})$$

Since the determinant $\Delta_1(E)$ is not affected by the substitution $E \rightarrow -E$, equation (A.7) gives, in general, n doubly degenerate nonnegative roots E_j ($j = 1, 2, \dots, n$). Consequently, we obtain n spin-wave modes with energies

$$\varepsilon_j(\mathbf{k}) = 2E_j,$$

which makes it possible to write \mathcal{H}_2 in the form (1.23), where, according to (A.4),

$$\Delta \mathcal{H}_0 = - \sum_{t, s, k} E_s |v_{ts}|^2. \quad (\text{A.8})$$

The convenience of the second quantization method lies in the fact that it allows us, if the coefficients of the quadratic terms $\alpha_{jj'}$ and $\beta_{jj'}$ are known, to write immediately the equation

$$\Delta_1(E) = 0, \quad (\text{A.9})$$

which gives the spin-wave spectrum.

II. ACOUSTICAL AND OPTICAL MODES

We shall now consider the problem of the number of “acoustical” and “optical” modes using, for simplicity, the classical equations of motion for the sublattice magnetic moments. Since we are interested only in the absence or presence of energy gaps due to exchange forces, we need to retain in the Hamiltonian only the exchange terms and, moreover, we can restrict ourselves to uniform oscillations of the vectors \mathbf{M}_j (corresponding to the wave vector $\mathbf{k} = 0$). Under these conditions

$$\mathcal{H} = \frac{1}{2} A_{jj'} \mathbf{M}_j \mathbf{M}_{j'} \quad (\text{A.10})$$

and the equations of motion (1.18) become

$$\left(\frac{1}{\gamma_j} \right) \dot{\mathbf{M}}_j = [\mathbf{M}_j \cdot A_{jj'} \mathbf{M}_{j'}]. \quad (\text{A.11})$$

(The double “dummy” indices indicate summation.)

Let us assume that at equilibrium the magnetic moments are directed along a common axis \mathbf{Z} (collinear magnetic structures). We shall consider small oscillations of \mathbf{M}_j about this axis. Introducing new variables

$$M_j^\pm = M_{jx} \pm iM_{jy},$$

we find from (A.11)

$$\left(\frac{\omega}{\gamma_j} \right) M_j^\pm = \mp (A_{jj'} M_{j'}) M_j^\pm \pm (A_{jj'} M_j) M_{j'}^\pm,$$

where $M_j = M_{jz}$. These two systems of equations may be written more simply:

$$(\alpha_{jj'} \pm \omega \delta_{jj'}) \sigma_{j'}^\pm = 0, \quad (\text{A.12})$$

where

$$\begin{aligned} \sigma_j^\pm &= \frac{M_j^\pm}{M_j}, & \alpha_{jj} &= - \sum_{j' \neq j} B_{jj'} S_{j'}, & B_{jj'} &= \gamma_j A_{jj} \gamma_{j'}. \\ S_j &= \frac{M_j}{\gamma_j}, & \alpha_{jj'} &= B_{jj'} S_{j'} \quad (j' \neq j), \end{aligned}$$

It is easily found that

$$\sum_{j'} \alpha_{jj'} = 0. \quad (\text{A.13})$$

If the systems of equations (A.12) have nonzero solutions for σ_j^\pm , their determinants should be zero:

$$\|\alpha_{jj'} \pm \omega \delta_{jj'}\| = 0. \quad (\text{A.14})$$

Thus we obtain two equations, each of the n th degree, to determine the eigenfrequencies of oscillations of a system of n magnetic moments. The solutions of these equations differ only by their sign and therefore we have, in general, n nonnegative roots giving n modes of the spectrum. The number of "acoustical" modes is obviously equal to the number of roots $\omega = 0$ of one of the equations.

Expanding the determinant (A.14), the equation (for example, in the case of a plus sign in front of ω) may be represented in the form

$$\omega^n + D_1 \omega^{n-1} + \dots + D_{n-1} \omega + D_n = 0, \quad (\text{A.15})$$

where

$$D_n = \|a_{jj}\|, \quad (\text{A.16})$$

and D_{n-p} is the sum of all the determinants of the $(n-p)$ -th order, obtained from the determinant D_n by crossing out p columns and p rows with the same number (i.e., intersecting at elements a_{jj}).

If we add to one of the columns of the determinant in (A.16) all the remaining columns, we then obtain, according to (A.13), a column of zeros; consequently, we always get

$$D_n \equiv 0. \quad (\text{A.17})$$

However, this yields the trivial result that in every magnetic material there is at least one oscillation made without an energy gap (in the absence of an external field and magnetic anisotropy forces). This is the "acoustical" mode.

If we divide by ω and take into account (A.17), the free term in (A.15) is then D_{n-1} . We can show that D_{n-1} is proportional to the expression

$$\sum_{j=1}^n S_j = S_0,$$

which represents the total angular momentum of a magnetic substance, associated with the sublattice magnetic moments.* The

*The relationship $D_{n-1} \sim \sum S_j$ has been checked for special cases, when $n = 2, 3$, and 4. However, there is no doubt that it can be generalized to any value of n .

next coefficient D_{n-2} is, in general, always different from zero and we cannot isolate from it the factor S_0 .

Thus, if $S_0 \neq 0$ (ferromagnetism), there is a single root $\omega = 0$, while if $S_0 = 0$ (antiferromagnetism) there are two such roots. The values of all the remaining roots $\omega \neq 0$, corresponding to the "optical" modes of the oscillation spectrum, are determined by the energy of exchange interactions between magnetic sublattices.

We shall illustrate this for the case of three magnetic sublattices ($n = 3$). In this case

$$\begin{aligned} \alpha_{11} &= -B_{12}S_2 - B_{13}S_3, & \alpha_{12} &= B_{12}S_2, & \alpha_{21} &= B_{21}S_1, \\ \alpha_{22} &= -B_{21}S_1 - B_{23}S_3, & \alpha_{13} &= B_{13}S_3, & \alpha_{31} &= B_{31}S_1, \\ \alpha_{33} &= -B_{31}S_1 - B_{32}S_2, & \alpha_{23} &= B_{23}S_3, & \alpha_{32} &= B_{32}S_2. \end{aligned}$$

We note that $B_{jj'} = B_{j'j}$. Then, bearing in mind that $D_3 \equiv 0$ and after extracting one root $\omega = \omega_1 = 0$, Eq. (A.15) becomes

$$\omega^2 = D_1\omega + D_2 = 0,$$

where

$$D_2 = \begin{vmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{vmatrix} + \begin{vmatrix} \alpha_{11} & \alpha_{13} \\ \alpha_{31} & \alpha_{33} \end{vmatrix} + \begin{vmatrix} \alpha_{22} & \alpha_{23} \\ \alpha_{32} & \alpha_{33} \end{vmatrix}$$

and

$$D_1 = \alpha_{11} + \alpha_{22} + \alpha_{33}.$$

Direct calculation of D_2 and D_1 gives:

$$\begin{aligned} D_2 &= (S_1 + S_2 + S_3) (B_{12}B_{13}S_1 + B_{12}B_{23}S_2 + B_{13}B_{23}S_3), \\ D_1 &= -B_{12}(S_1 + S_2) - B_{13}(S_1 + S_3) - B_{23}(S_2 + S_3). \end{aligned}$$

Thus, if $S_1 + S_2 + S_3 \neq 0$, we have only one "acoustical" root, $\omega_1 = 0$, and two "optical" roots, $\omega_2 \neq 0$ and $\omega_3 \neq 0$. If $S_1 + S_2 + S_3 = 0$, there are two "acoustical" modes and one "optical" mode:

$$\omega_3 = -D_1 = -B_{12}S_3 - B_{13}S_2 - B_{23}S_1 \neq 0.$$

In conclusion, we note that the antiferromagnetic state with $\sum S_i = 0$ permits the existence of a nonzero magnetic moment due to the difference between the magnetomechanical ratios γ_i of different sublattices.

Appendix B

ENERGY OF ZERO-POINT OSCILLATIONS OF A FERROMAGNET

We shall consider in detail the role of the zero-point oscillation energy $\Delta\mathcal{H}_0$ related to the magnetocrystalline anisotropy of ferromagnets. At the same time, we shall present a modified method for calculating the spin-wave energy which does not require the assumption that magnetization gradients are small and, consequently, that the wave vector \mathbf{k} is small, which may be important in calculating $\Delta\mathcal{H}_0$.

The summation in (2.6) is carried out for all values of \mathbf{k} , but, in contrast to the sum in (2.27), we cannot explicitly separate the factor which cuts off the contribution of the terms with higher values of \mathbf{k} . In the sum (2.27), the distribution function \bar{n}_k acted as such a cutoff factor.

The Hamiltonian for a uniaxial ferromagnet (ignoring the magnetostatic energy) may be written in a form more general than (2.1):

$$\begin{aligned} \mathcal{H} = & - \int A(\mathbf{r} - \mathbf{r}') \mathbf{m}(\mathbf{r}) \mathbf{m}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' - \\ & - \int K(\mathbf{r} - \mathbf{r}') m_z(\mathbf{r}) m_z(\mathbf{r}') d\mathbf{r} d\mathbf{r}' - H \int \mathbf{M}(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (\text{B.1})$$

We shall assume that the axis of easy magnetization coincides with the crystal axis and that the magnetic field is applied at right angles to that axis, i.e., $H = H_x$. The expression in (2.6) shows that when $K > 0$, we should expect the largest value of $\Delta\mathcal{H}_0$ for $H \perp \mathbf{Z}$.

After introducing the second quantization operators b_r and b_r^\dagger , the Hamiltonian of (B.1) may be reduced again to the form (1.20), where

$$\begin{aligned} \frac{\mathcal{H}_0}{V} = & -A - \left(\frac{\mu}{M_0}\right) A(0) - \\ & - K \cos^2 \theta - \frac{1}{2} \left(\frac{\mu}{M_0}\right) K(0) \sin^2 \theta - H M_0 \sin \theta, \end{aligned} \quad (\text{B.2})$$

$$\mathcal{H}_2 = \int d\mathbf{r} d\mathbf{r}' \left[\alpha(\mathbf{r} - \mathbf{r}') \dot{b}_r \dot{b}_{r'} + \frac{1}{2} \beta(\mathbf{r} - \mathbf{r}') (b_r \dot{b}_{r'} + \dot{b}_r b_{r'}) \right], \quad (\text{B.3})$$

$$\alpha(\mathbf{r} - \mathbf{r}') = \left(\frac{2\mu}{M_0} \right) \left[A \delta(\mathbf{r} - \mathbf{r}') - A(\mathbf{r} - \mathbf{r}') + \right. \\ \left. + K \cos^2 \theta \delta(\mathbf{r} - \mathbf{r}') - \frac{1}{2} K(\mathbf{r} - \mathbf{r}') \sin^2 \theta \right] + \mu H \sin \theta \delta(\mathbf{r} - \mathbf{r}'), \quad (\text{B.4})$$

$$\beta(\mathbf{r} - \mathbf{r}') = \left(\frac{\mu}{M_0} \right) K(\mathbf{r} - \mathbf{r}') \sin^2 \theta, \quad (\text{B.5})$$

$$A = \int A(\mathbf{r}) d\mathbf{r}, \quad K = \int K(\mathbf{r}) d\mathbf{r}. \quad (\text{B.6})$$

The two possibilities mentioned in Sec. 1 are:

1) $K(\mathbf{r}) = K \delta(\mathbf{r})$ ("local anisotropy" due to, for example, spin-orbital interaction in an atom);

2) $K(0) = 0$ ("correlation anisotropy" due to magnetic interactions between different atoms in a lattice).

We shall consider here only the latter anisotropy and, therefore, we shall assume that $K(0) = 0$ and $A(0) = 0$, which follows from the meaning of the exchange interaction itself.

Diagonalization of the quadratic form (B.3) is carried out using the following transformation:

$$b_r = \sum_k (\xi_k u_{rk} + \xi_k^* v_{rk}^*), \quad \dot{b}_r = \sum_k (\xi_k^* u_{rk}^* + \xi_k v_{rk}). \quad (\text{B.7})$$

The transformation coefficients u_{rk} and v_{rk} satisfy the system of equations

$$E u_{rk} = \int \alpha(\mathbf{r} - \mathbf{r}') u_{r'k} d\mathbf{r}' + \int \beta(\mathbf{r} - \mathbf{r}') v_{r'k} d\mathbf{r}', \\ -E v_{rk} = \int \alpha(\mathbf{r} - \mathbf{r}') v_{r'k} d\mathbf{r}' + \int \beta(\mathbf{r} - \mathbf{r}') u_{r'k} d\mathbf{r}' \quad (\text{B.8})$$

for the normalization condition

$$\int (|u_{rk}|^2 + |v_{rk}|^2) d\mathbf{r} = 1 \quad (\text{B.9})$$

and so on (cf. Appendix A.I).

The system of equations in (B.8) is solved by means of the substitution:

$$u_{rk} = \frac{1}{\sqrt{V}} U_k e^{ikr}, \quad v_{rk} = \frac{1}{\sqrt{V}} V_k e^{ikr}, \quad (\text{B.10})$$

which gives new equations

$$(\alpha_k - E) U_k + \beta_k V_k = 0, \\ \beta_k U_k + (\alpha_k + E) V_k = 0, \quad (\text{B.11})$$

where

$$\begin{aligned}\alpha_k &= \left(\frac{2\mu}{M_0}\right) \int d\mathbf{r} \left\{ A(\mathbf{r}) (1 - e^{ikr}) + \right. \\ &\quad \left. + K(\mathbf{r}) (\cos^2 \theta - \frac{1}{2} \sin^2 \theta e^{ikr}) \right\} + \mu H \sin \theta, \\ \beta_k &= \left(\frac{\mu}{M_0}\right) \sin^2 \theta \int K(\mathbf{r}) e^{ikr} d\mathbf{r}.\end{aligned}\quad (\text{B.12})$$

From the condition of the solvability of the system (B.11), we find the spin-wave energy

$$\varepsilon_k \equiv E = \sqrt{\alpha_k^2 - |\beta_k|^2}.$$

Using the normalization condition

$$U_k^2 - V_k^2 = 1,$$

we obtain

$$V_k^2 = \frac{1}{2} \frac{\alpha_k^2 - \sqrt{\alpha_k^2 - \beta_k^2}}{\varepsilon_k}.$$

The total energy of the system is

$$\mathcal{H} = \mathcal{H}_0 + \Delta\mathcal{H}_0 + \sum_k \varepsilon_k n_k,$$

where

$$\Delta\mathcal{H}_0 = -\frac{1}{2} \sum_k (\alpha_k^2 - \sqrt{\alpha_k^2 - \beta_k^2}). \quad (\text{B.13})$$

To calculate $\Delta\mathcal{H}_0$, it is more convenient to use the discrete model of a spin lattice, obtained by the substitution

$$A(\mathbf{r}) = \sum_k A(\mathbf{R}_n) \delta(\mathbf{r} - \mathbf{R}_n), \quad K(\mathbf{r}) = \sum_n K(\mathbf{R}_n) \delta(\mathbf{r} - \mathbf{R}_n)$$

(\mathbf{R}_n are the radius vectors of the lattice sites).

Since we wish to determine only the upper limit of the quantity $\Delta\mathcal{H}_0$, we shall consider a simple tetragonal lattice and use the nearest-neighbor approximation for $A(\mathbf{r})$ and $K(\mathbf{r})$.

Let us assume that for the nearest neighbors in the basal plane (parameter a_\perp), $A(\mathbf{R}_n) = A_\perp$, $K(\mathbf{R}_n) = K_\perp$, and in the direction of the crystal axis (parameter a_z), $A(\mathbf{R}_n) = A_z$ and $K(\mathbf{R}_n) = K_z$. At

equilibrium, the magnetization vector ($H = H_A \sin \theta$) is then given, instead of (B.12), by

$$\alpha_k = \left(\frac{2\mu}{M_0}\right) [A'_\perp (1 - \cos a_\perp k_x) + A'_\perp (1 - \cos a_\perp k_y) + A'_z (1 - \cos a_z k_z)] + \mu H_A \left(\cos^2 \theta + \frac{1}{2} \sin^2 \theta\right), \quad (\text{B.14})$$

$$\beta_k = \frac{1}{2} \mu H_A \sin^2 \theta - \left(\frac{2\mu}{M_0}\right) [K_\perp (1 - \cos a_\perp k_\perp) + K_z (1 - \cos a_z k_z)] \sin^2 \theta, \quad (\text{B.15})$$

where

$$A'_\perp = A_\perp + K_\perp \sin^2 \theta, \quad A'_z = A_z + K_z \sin^2 \theta, \quad H_A = \frac{2K}{M_0}.$$

The summation in (B.13) is within the first Brillouin zone

$$-\pi \leq a_\alpha k_\alpha \leq \pi. \quad (\text{B.16})$$

We shall introduce the following expressions

$$f_k = \left(\frac{2\mu}{M_0}\right) \left(\frac{A}{\pi^2}\right) (a_\perp^2 k_\perp^2 + a_z^2 k_z^2) + \rho, \quad \rho = \frac{1}{2} \mu H_A \sin^2 \theta,$$

where $A = \min(A_\perp, A_z)$. It is easily seen that in the region defined by (B.16) $f_k < \alpha_k$, $\rho > \beta_k$. Therefore, if we replace α_k with f_k and β_k with ρ in (B.13), this can only increase the absolute value of $\Delta \mathcal{H}_0$, i.e.,

$$|\Delta \mathcal{H}_0| < \frac{1}{2} \sum_k (f_k - \sqrt{f_k^2 - \rho^2}). \quad (\text{B.17})$$

We shall now change from summation over k to integration with respect to $g_x = a_\perp k_x$, $g_y = a_\perp k_y$, $g_z = a_z k_z$. The integration domain will be taken to be the g space bounded by a sphere of radius $\sqrt{3}\pi$, which includes the region (B.16). Since the integrand is positive, the extension of the integration domain can only strengthen the inequality (B.17) so that we have

$$|\Delta \mathcal{H}_0| < \frac{N}{4\pi^2} \int_0^{3\pi^2} (f_g - \sqrt{f_g^2 - \rho^2}) g^2 dg.$$

Calculating explicitly the above integral, we finally obtain

$$|\Delta \mathcal{H}_0| < \frac{\sqrt{3}\pi}{40} H_A (N\mu) \frac{H_A}{H_E} \sin^4 \theta,$$

where $H_E = 2A/M_0$. Comparing the above inequality with the part of \mathcal{H}_0 which depends on θ ,

$$\mathcal{H}_0(\theta) = H_A M_0 V \sin^2 \theta / 2,$$

we see that, in fact, we always have

$$\left| \frac{\Delta \mathcal{H}_0}{\mathcal{H}_0(\theta)} \right| < \frac{H_A}{H_E} \ll 1.$$

Therefore, the relative contribution of $\Delta \mathcal{H}_0$ to the magnetization is also small.

Appendix C

I. ANISOTROPY CONSTANTS AND MODULUS OF THE MAGNETIZATION VECTOR

Without assuming a state of magnetic saturation, the anisotropy constants at a temperature T can be found simply from the thermodynamic potential of a system in the following way. We shall define an effective magnetic field acting on the magnetization of a ferromagnet:

$$H_{\text{eff}} = - \frac{1}{M} \frac{\partial \Omega}{\partial \alpha} . \quad (\text{C.1})$$

This field has a definite physical meaning: it is proportional to the experimentally measured (in determining anisotropy constants) moment of the forces acting on the system.

According to (2.24) and (3.6), when the condition (3.24) applies, we have

$$H_{\text{eff}} = H - \frac{1}{M} \sum_N \frac{\partial f_N}{\partial \alpha} \left[1 - \frac{\mu}{M_0 V} N (2N + 1) \sum_k \bar{n}_k \right] . \quad (\text{C.2})$$

On the other hand, the magnetization of the system at T is

$$M(T) = - \frac{\partial \Omega}{\partial H} = M_0 \alpha \left(1 - \frac{\mu}{M_0 V} \sum_k \bar{n}_k \right) . \quad (\text{C.3})$$

Comparing (C.2) with (C.3) and using (3.26), we again obtain a formula of the (3.27) type in which now $M(T)$ is not the saturation magnetization but the modulus of the magnetization vector at a temperature T . In the absence of saturation (when the angle between \mathbf{M} and \mathbf{H} is not zero) we usually determine experimentally the projection of the vector \mathbf{M} along the direction of \mathbf{H} and not the modulus M itself. Therefore, the above general formula is difficult to check experimentally.

II. HARMONIC FORM OF THE MAGNETOCRYSTALLINE ENERGY

We shall now give a harmonic expansion for the free energy of the anisotropy of crystals of various symmetries, which includes terms necessary for practical application.

Cubic crystals:*

$$\begin{aligned}
 F_A = & \bar{K}_2 [\alpha_x^4 + \alpha_y^4 + \alpha_z^4 - 3(\alpha_x^2 \alpha_y^2 + \alpha_x^2 \alpha_z^2 + \alpha_y^2 \alpha_z^2)] + \\
 & + \bar{K}_3 \left[\alpha_x^6 + \alpha_y^6 + \alpha_z^6 - \frac{15}{2} (\alpha_x^4 \alpha_y^2 + \alpha_x^2 \alpha_y^4 + \alpha_x^4 \alpha_z^2 + \right. \\
 & \quad \left. + \alpha_x^2 \alpha_z^4 + \alpha_y^2 \alpha_z^4 + \alpha_y^4 \alpha_z^2) + 90 \alpha_x^2 \alpha_y^2 \alpha_z^2 \right] + \\
 & + \bar{K}_4 [\alpha_x^8 + \alpha_y^8 + \alpha_z^8 - 14 (\alpha_x^6 \alpha_y^2 + \alpha_y^6 \alpha_x^2 + \\
 & \quad + \alpha_x^6 \alpha_z^2 + \alpha_z^6 \alpha_x^2 + \alpha_y^6 \alpha_z^2 + \alpha_z^6 \alpha_y^2) + \\
 & \quad + 35 (\alpha_x^4 \alpha_y^4 + \alpha_x^4 \alpha_z^4 + \alpha_y^4 \alpha_z^4)].
 \end{aligned} \tag{C.5}$$

Uniaxial crystals—general terms:

$$\begin{aligned}
 F_A = & \bar{K}_1 (\alpha_x^2 + \alpha_y^2 - 2\alpha_z^2) + \\
 & + \bar{K}_2 \left[(\alpha_x^2 + \alpha_y^2)^2 - 8 (\alpha_x^2 + \alpha_y^2) \alpha_z^2 + \frac{8}{3} \alpha_z^4 \right].
 \end{aligned} \tag{C.6}$$

In addition to these terms, various uniaxial crystals have terms which allow for the anisotropy in the basal plane.

Tetragonal crystals:

$$\bar{K}_2' \left[\alpha_x^2 \alpha_y^2 - \frac{1}{6} (\alpha_x^4 + \alpha_y^4) \right]. \tag{C.7}$$

Hexagonal crystals [64]:

$$\bar{K}_3 \alpha_x \alpha_y \left(\alpha_x^4 - \frac{10}{3} \alpha_x^2 \alpha_y^2 + \alpha_y^4 \right) \equiv f_3. \tag{C.8}$$

Rhombohedral crystals:

$$\bar{K}_2 \alpha_x \alpha_z (\alpha_x^2 - 3\alpha_y^2) \equiv f_3. \tag{C.9}$$

III. MAGNETOELASTIC ENERGY (CUBIC CRYSTALS)

The standard form of the magnetoelastic energy is:

$$\begin{aligned}
 F_{me} = & \lambda_1^{(1)} (\sigma_{xx} \alpha_x^2 + \sigma_{yy} \alpha_y^2 + \sigma_{zz} \alpha_z^2) + \\
 & + 2\lambda_1^{(2)} (\sigma_{xy} \alpha_x \alpha_y + \sigma_{xz} \alpha_x \alpha_z + \sigma_{yz} \alpha_y \alpha_z) + \\
 & + \lambda_2^{(1)} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) (\alpha_x^2 \alpha_y^2 + \alpha_x^2 \alpha_z^2 + \alpha_y^2 \alpha_z^2) + \\
 & + \lambda_2^{(2)} (\sigma_{xx} \alpha_x^4 + \sigma_{yy} \alpha_y^4 + \sigma_{zz} \alpha_z^4) + \\
 & + 2\lambda_2^{(3)} (\sigma_{xy} \alpha_x \alpha_y \alpha_z^2 + \sigma_{yz} \alpha_x^2 \alpha_y \alpha_z + \sigma_{xz} \alpha_x \alpha_y^2 \alpha_z).
 \end{aligned} \tag{C.10}$$

*[The numbering of equations follows the Russian text; (C.4) was omitted.—Ed.]

A possible harmonic form of F_{me} accurate to terms of the fourth degree in α (i.e., up to $N = 2$) is

$$\begin{aligned}
 F_{\text{me}} = & \frac{1}{2} \lambda_1^{(1)} [\sigma_{xx} (2\alpha_x^2 - \alpha_y^2 - \alpha_z^2) + \\
 & + \sigma_{yy} (2\alpha_y^2 - \alpha_x^2 - \alpha_z^2) + \sigma_{zz} (2\alpha_z^2 - \alpha_x^2 - \alpha_y^2)] + \\
 & + 2\lambda_2^{(1)} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) [\alpha_x^4 + \alpha_y^4 + \alpha_z^4 - 3(\alpha_x^2\alpha_y^2 + \alpha_x^2\alpha_z^2 + \\
 & + \alpha_y^2\alpha_z^2)] + \lambda_2^{(2)} \{ \sigma_{xx} [\alpha_x^4 - 3(\alpha_x^2\alpha_y^2 + \alpha_x^2\alpha_z^2 - \alpha_y^2\alpha_z^2)] + \\
 & + \sigma_{yy} [\alpha_y^4 - 3(\alpha_x^2\alpha_y^2 + \alpha_y^2\alpha_z^2 - \alpha_x^2\alpha_z^2)] + \sigma_{zz} [\alpha_z^4 - \\
 & - 3(\alpha_x^2\alpha_z^2 + \alpha_y^2\alpha_z^2 - \alpha_x^2\alpha_y^2)] \} + 2\lambda_2^{(3)} \{ \sigma_{xy}\alpha_x\alpha_y \left[\alpha_z^2 - \right. \\
 & - \left. \frac{1}{6}(\alpha_x^2 + \alpha_y^2) \right] + \sigma_{xz}\alpha_x\alpha_z \left[\alpha_y^2 - \frac{1}{6}(\alpha_x^2 + \alpha_z^2) \right] + \\
 & + \sigma_{yz}\alpha_y\alpha_z \left[\alpha_x^2 - \frac{1}{6}(\alpha_y^2 + \alpha_z^2) \right] \} .
 \end{aligned} \tag{C.11}$$

The lower index of λ gives the order of the constant N , and the upper index distinguishes between various constants of the same order.

Appendix D

I. SPIN-WAVE ENERGY (GENERAL CASE)

Let us assume that the equilibrium classical vectors $M_{10} = m_{10}M_0/2$ and $M_{20} = m_{20}M_0/2$ lie in the same plane as Z and H , which we shall take to be the YZ plane (Fig. 5). The transformation given in (1.18) from natural systems of coordinates $X_jY_jZ_j$ (in which the quantization axes m_{j0} for the sublattice magnetizations $M_j(\mathbf{r})$ coincide with the Z_j axes) to a general system of coordinates XYZ (which are related to the crystal axes), can be represented by

$$\begin{aligned} M_{jx} &= M_{jx_j}, \\ M_{jy} &= M_{jy_j} \cos \theta_j - M_{jz_j} \sin \theta_j, \\ M_{jz} &= M_{jz_j} \cos \theta_j + M_{jy_j} \sin \theta_j. \end{aligned} \tag{D.1}$$

Here, θ_j are the angles between the axes Z and Z_j , related in the following way to the ground-state parameters θ and m :

$$\begin{aligned} \sin \theta_1 &= \sqrt{1-m^2} \sin \theta - m \cos \theta, \\ \sin \theta_2 &= -\sqrt{1-m^2} \sin \theta - m \cos \theta. \end{aligned} \tag{D.2}$$

Using (D.1), (D.2), (1.15), and (1.19), we can find from the Hamiltonian in (4.4) the quadratic form of \mathcal{H}_2 (in which the Bose operators $b_k^{(1)}$ and $b_k^{(2)}$ are quadratic):

$$\begin{aligned} \mathcal{H}_2(\mathbf{k}) &= \alpha_1 b_k^{(1)\dagger} b_k^{(1)} + \alpha_2 b_k^{(2)\dagger} b_k^{(2)} + \alpha_3 (b_k^{(1)\dagger} b_k^{(2)} + b_k^{(2)\dagger} b_k^{(1)}) + \\ &+ \frac{1}{2} \beta_1 b_k^{(1)\dagger} b_{-k}^{(1)} + \frac{1}{2} \beta_1^* b_k^{(1)} b_{-k}^{(1)} + \frac{1}{2} \beta_2 b_k^{(2)\dagger} b_{-k}^{(2)} + \frac{1}{2} \beta_2^* b_k^{(2)} b_{-k}^{(2)} + \\ &+ \frac{1}{2} \beta_3 (b_k^{(1)\dagger} b_{-k}^{(2)} + b_k^{(2)\dagger} b_{-k}^{(1)}) + \frac{1}{2} \beta_3^* (b_k^{(1)} b_{-k}^{(2)} + b_k^{(2)} b_{-k}^{(1)}), \end{aligned} \tag{D.3}$$

where

$$\begin{aligned}
 \alpha_1 &= \left(\frac{\mu}{2M_0}\right) \left[(1-2m^2) A + A_k + B_k + (\cos^2 \theta - m^2) (a-b) - \right. \\
 &\quad \left. - (l \cos \theta + m \sin \theta)^2 (a+b) + \frac{1}{2} (l \sin \theta - m \cos \theta)^2 (a+b) - \right. \\
 &\quad \left. - 2 (l \sin \theta - m \cos \theta) h_y + 2 (l \cos \theta + m \sin \theta) h_z + 2\pi M_0^2 k_1^- \frac{k_1^+}{k^2} \right], \\
 \alpha_2 &= \left(\frac{\mu}{2M_0}\right) \left[(1-2m^2) A + A_k + B_k + (\cos^2 \theta - m^2) (a-b) - \right. \\
 &\quad \left. - (l \cos \theta - m \sin \theta)^2 (a+b) + \frac{1}{2} (l \sin \theta + m \cos \theta)^2 (a+b) + \right. \\
 &\quad \left. + 2 (l \sin \theta + m \cos \theta) h_y - 2 (l \cos \theta - m \sin \theta) h_z + 2\pi M_0^2 k_2^- \frac{k_2^+}{k^2} \right], \\
 \alpha_3 &= \left(\frac{\mu}{2M_0}\right) \left[m^2 (A + A_k - B_k) - \frac{1}{2} (\sin^2 \theta - m^2) (a-b) + \right. \\
 &\quad \left. + 2\pi M_0^2 k_1^- \frac{k_2^+}{k^2} \right], \\
 \beta_1 &= \left(\frac{\mu}{2M_0}\right) \left[-\frac{1}{2} (l \sin \theta - m \cos \theta)^2 (a+b) + 2\pi M_0^2 \left(\frac{k_1^-}{k}\right)^2 \right], \\
 \beta_2 &= \left(\frac{\mu}{2M_0}\right) \left[-\frac{1}{2} (l \sin \theta + m \cos \theta)^2 (a+b) + 2\pi M_0^2 \left(\frac{k_2^-}{k}\right)^2 \right], \\
 \beta_3 &= \left(\frac{\mu}{2M_0}\right) \left[(1-m^2) (A + A_k - B_k) + \frac{1}{2} (\sin^2 \theta - m^2) (a-b) + \right. \\
 &\quad \left. + 2\pi M_0^2 k_1^- \frac{k_2^-}{k^2} \right], \quad k_j^\pm = k_{xj} \pm i k_{yj}.
 \end{aligned}$$

It follows from Appendix A that, on diagonalization of (D.3), we obtain the following equation for determining the spin-wave energy $\varepsilon = \varepsilon(k)$:

$$\begin{vmatrix}
 \alpha_1 - \varepsilon & \alpha_3 & \beta_1 & \beta_3 \\
 \alpha_3^* & \alpha_2 - \varepsilon & \beta_3 & \beta_2 \\
 \beta_1^* & \beta_3^* & \alpha_1 + \varepsilon & \alpha_3^* \\
 \beta_3^* & \beta_2^* & \alpha_3 & \alpha_2 + \varepsilon
 \end{vmatrix} = 0. \quad (D.4)$$

The solution of the above equation gives two roots for ε :

$$\varepsilon_k^{(1,2)} = (P \pm \sqrt{R})^{1/2}, \quad (D.5)$$

where

$$\begin{aligned}
 P &= \frac{1}{2} (\alpha_1^2 + \alpha_2^2 + 2|\alpha_3|^2) - \frac{1}{2} (|\beta_1|^2 + |\beta_2|^2 + 2|\beta_3|^2), \\
 R &= \frac{1}{4} [(\alpha_1^2 - \alpha_2^2) - (|\beta_1|^2 - |\beta_2|^2)]^2 - |\beta_3|^2 (\alpha_1 - \alpha_2)^2 - \\
 &\quad - |\beta_1^* \alpha_3 - \beta_2^* \alpha_3^*|^2 + |\alpha_2 \alpha_3^* - \beta_3 \beta_1^*|^2 + |\alpha_1 \alpha_3 - \beta_3 \beta_2^*|^2 + \\
 &\quad + [(\alpha_1 \alpha_3^* - \beta_3 \beta_1^*) (\alpha_2 \alpha_3 - \beta_3 \beta_2^*) + \text{complex conjugates}].
 \end{aligned}$$

II. TRANSFORMATION COEFFICIENTS AND $\Delta\mathcal{H}_0$

The system of equations for determining the coefficients of the diagonalization transformation (A.3) has the following form:

$$\begin{aligned} (\alpha_1 - \varepsilon) u_1 + \alpha_3 u_2 + \beta_1 v_1 + \beta_3 v_2 &= 0, \\ \alpha_3^* u_1 + (\alpha_2 - \varepsilon) u_2 + \beta_3 v_1 + \beta_2 v_2 &= 0, \\ \beta_1^* u_1 + \beta_3^* u_2 + (\alpha_1 + \varepsilon) v_1 + \alpha_3^* v_2 &= 0, \\ \beta_3^* u_1 + \beta_2^* u_2 + \alpha_3 v_1 + (\alpha_2 + \varepsilon) v_2 &= 0. \end{aligned} \quad (\text{D.6})$$

We shall first find the coefficients u and v , and then the zero-point oscillation energy (A.8) for some special cases.

The (z/\parallel) state. Excluding the magnetostatic energy, we have for this state ($\theta = m = 0$)

$$\begin{aligned} \alpha_{1,2} &= \alpha \pm \mu H, \quad \alpha = \left(\frac{\mu}{2M_0} \right) (A + A_k + B_k - 2b), \\ \beta_1 &= \beta_2 = \alpha_3 = 0, \quad \beta_3 = \left(\frac{\mu}{2M_0} \right) (A + A_k - B_k). \end{aligned} \quad (\text{D.7})$$

Consequently, the system (D.6) splits into two subsystems:

$$\begin{aligned} \text{I. } & \begin{cases} [\alpha - (\varepsilon - \mu H)] u_1 + \beta_3 v_2 = 0, \\ \beta_3 u_1 + [\alpha + (\varepsilon - \mu H)] v_2 = 0; \end{cases} \\ \text{II. } & \begin{cases} [\alpha - (\varepsilon + \mu H)] u_2 + \beta_3 v_1 = 0, \\ \beta_3 u_2 + [\alpha + (\varepsilon + \mu H)] v_1 = 0. \end{cases} \end{aligned} \quad (\text{D.8})$$

The first subsystem gives

$$\varepsilon_{1k} = \sqrt{\alpha^2 - \beta_3^2} + \mu H; \quad (\text{D.9})$$

the corresponding transformation coefficients are

$$u_{11} = U_1 \quad \text{and} \quad v_{21} = V_1.$$

From the second subsystem, we obtain

$$\begin{aligned} \varepsilon_{2k} &= \sqrt{\alpha^2 - \beta_3^2} - \mu H, \\ u_{22} &= U_2 \quad \text{and} \quad v_{12} = V_2. \end{aligned} \quad (\text{D.10})$$

From the orthonormalization conditions (A.6) we also get

$$U_1^2 - V_1^2 = 1, \quad U_2^2 - V_2^2 = 1. \quad (\text{D.11})$$

Solving the above equations in conjunction with (D.8), we find

$$\begin{aligned} V_1^2 = V_2^2 &= \frac{\alpha - \sqrt{\alpha^2 - \beta_3^2}}{2 \sqrt{\alpha^2 - \beta_3^2}} \equiv V_k^2, \\ U_1^2 = U_2^2 &= 1 + V_k^2 \equiv U_k^2. \end{aligned} \quad (\text{D.12})$$

The transformation which makes the expression (D.3)* diagonal, may now be written in the form

$$\begin{aligned} b_k^{(1)} &= U_k \xi_{1k} - V_k \xi_{2k}^+, \quad b_k^{(1)+} = U_k \xi_{1k}^+ - V_k \xi_{2k}, \\ b_{-k}^{(2)} &= U_k \xi_{2k} - V_k \xi_{1k}^+, \quad b_{-k}^{(2)+} = U_k \xi_{2k}^+ - V_k \xi_{1k}. \end{aligned} \quad (\text{D.13})$$

(The signs are selected so that $U_k V_k > 0$.)

The zero-point oscillation energy

$$\Delta \mathcal{H}_0 = - \sum_k |V_k|^2 (\varepsilon_{1k} + \varepsilon_{2k}) = - \sum_k [\alpha - \sqrt{\alpha^2 - \beta_3^2}] \quad (\text{D.14})$$

is independent of the magnetic field H .

The (y/\perp) state. Substituting into (D.3) $\theta = 0$, $h = m(A - b)$, we have

$$\begin{aligned} \alpha &= \alpha_1 = \alpha_2 = \left(\frac{\mu}{2M_0}\right) \left[A + A_k + B_k - 2b + \frac{1}{2} m^2 (a + b) \right], \\ \beta &= \beta_1 = \beta_2 = \left(\frac{\mu}{2M_0}\right) \left[-\frac{1}{2} m^2 (a + b) \right], \\ \alpha_3 &= \left(\frac{\mu}{2M_0}\right) m^2 \left[A + A_k - B_k + \frac{1}{2} (a - b) \right], \\ \beta_3 &= \left(\frac{\mu}{2M_0}\right) \left[(1 - m^2) (A + A_k - B_k) - \frac{1}{2} m^2 (a - b) \right]. \end{aligned} \quad (\text{D.15})$$

The coefficients u and v , according to (D.6) and (D.15), now satisfy the following system of equations

$$\begin{aligned} (\alpha - \varepsilon) u_1 + \alpha_3 u_2 + \beta v_1 + \beta_3 v_2 &= 0, \\ \alpha_3 u_1 + (\alpha - \varepsilon) u_2 + \beta_3 v_1 + \beta v_2 &= 0, \\ \beta u_1 + \beta_3 u_2 + (\alpha + \varepsilon) v_1 + \alpha_3 v_2 &= 0, \\ \beta_3 u_1 + \beta u_2 + \alpha_3 v_1 + (\alpha + \varepsilon) v_2 &= 0. \end{aligned} \quad (\text{D.16})$$

*This expression can be written in the present case only in terms of $b_k^{(1)}$, $b_k^{(1)+}$, $b_{-k}^{(2)}$, and $b_{-k}^{(2)+}$.

Adding and subtracting these equations in pairs, we obtain two independent subsystems

$$\begin{aligned} \text{I. } & \begin{cases} (\alpha + \alpha_3 - \varepsilon) (u_1 + u_2) + (\beta + \beta_3) (v_1 + v_2) = 0, \\ (\beta + \beta_3) (u_1 + u_2) + (\alpha + \alpha_3 + \varepsilon) (v_1 + v_2) = 0; \end{cases} \\ \text{II. } & \begin{cases} (\alpha - \alpha_3 - \varepsilon) (u_1 - u_2) + (\beta - \beta_3) (v_1 - v_2) = 0, \\ (\beta - \beta_3) (u_1 - u_2) + (\alpha - \alpha_3 + \varepsilon) (v_1 - v_2) = 0. \end{cases} \end{aligned} \quad (\text{D.17})$$

From the condition of the solvability of the first subsystem, we obtain the first spin-wave mode

$$\varepsilon_{1k} = [(\alpha + \alpha_3)^2 - (\beta + \beta_3)^2]^{1/2}. \quad (\text{D.18})$$

If $\varepsilon = \varepsilon_{1k}$, we find from the second subsystem (whose determinant is not equal to zero if $\varepsilon = \varepsilon_{1k}$) that

$$\begin{aligned} u_1 (\varepsilon_{1k}) &\equiv u_{11} = u_2 (\varepsilon_{1k}) \equiv u_{21} = U_1, \\ v_1 (\varepsilon_{1k}) &\equiv v_{11} = v_2 (\varepsilon_{1k}) \equiv v_{21} = V_1. \end{aligned} \quad (\text{D.19})$$

Conversely, if the determinant of the second subsystem is equal to zero, we then obtain

$$\varepsilon_{2k} = [(\alpha - \alpha_3)^2 - (\beta - \beta_3)^2]^{1/2}. \quad (\text{D.20})$$

In this case, the determinant of the first subsystem is also not equal to zero and therefore

$$\begin{aligned} u_1 (\varepsilon_{2k}) &\equiv u_{12} = -u_2 (\varepsilon_{2k}) \equiv -u_{22} = U_2, \\ v_1 (\varepsilon_{2k}) &\equiv v_{12} = -v_2 (\varepsilon_{2k}) \equiv -v_{22} = V_2. \end{aligned} \quad (\text{D.21})$$

The orthonormalization conditions (A.6) give in the present case

$$\begin{aligned} U_1^2 + U_2^2 - V_1^2 - V_2^2 &= 1, \\ U_1^2 - V_1^2 - U_2^2 + V_2^2 &= 0. \end{aligned}$$

Consequently,

$$U_1^2 - V_1^2 = U_2^2 - V_2^2 = \frac{1}{2}. \quad (\text{D.22})$$

Simultaneous solution of (D.17) and (D.22), using (D.19) and (D.21), yields

$$V_1^2 = \frac{\alpha + \alpha_3 - \varepsilon_{1k}}{4\varepsilon_{1k}}, \quad V_2^2 = \frac{\alpha - \alpha_3 - \varepsilon_{2k}}{4\varepsilon_{2k}}. \quad (\text{D.23})$$

The transformation which makes \mathcal{H}_2 diagonal is then,

$$\begin{aligned} b_k^{(1)} &= \xi_k^{(1)} U_1 + \xi_k^{(2)} U_2 - \xi_{-k}^{(1)} V_1 + \xi_{-k}^{(2)} V_2, \\ b_k^{(2)} &= \xi_k^{(1)} U_1 - \xi_k^{(2)} U_2 - \xi_{-k}^{(1)} V_1 - \xi_{-k}^{(2)} V_2 \\ (U_1 V_1 > 0, \quad U_2 V_2 > 0) \text{ etc.} \end{aligned} \quad (\text{D.24})$$

The zero-point oscillation energy is given by the following expression:

$$\begin{aligned} \Delta \mathcal{H}_0 &= - \sum_k [\varepsilon_{1k} (v_{11}^2 + v_{21}^2) + \varepsilon_{2k} (v_{12}^2 + v_{22}^2)] = \\ &= - \frac{1}{2} \sum_k [2\alpha(k) - (\varepsilon_{1k} + \varepsilon_{2k})]. \end{aligned} \quad (\text{D.25})$$

III. LONGITUDINAL MAGNETIZATION OF AN ANTIFERROMAGNET BY A TRANSVERSE CIRCULARLY POLARIZED MAGNETIC FIELD

Ferromagnets exhibit a nonlinear resonance reduction of the longitudinal magnetization M_z by a transverse high-frequency magnetic field [142]. The order of magnitude of this effect at resonance is given by the expression

$$\frac{\Delta M_z}{M_z} = - \left(\frac{h_0}{\Delta H} \right)^2, \quad (\text{D.26})$$

where h_0 is the amplitude of the high-frequency field, and ΔH is the resonance linewidth. A similar effect should occur in antiferromagnets where a circularly polarized high-frequency field, perpendicular to the antiferromagnetic axis Z , may give rise to a steady component of the magnetization along this axis even in the absence of a steady magnetizing field ($H = H_z = 0$). It is interesting to estimate the order of magnitude of this effect.

The thermodynamic potential term, important in antiferromagnetic resonance in a uniform high-frequency field, is, for uniaxial crystals,

$$\Phi = \frac{1}{2} A m^2 + \frac{1}{2} a m_z^2 + \frac{1}{2} b l_z^2 - M m h,$$

where $m = (M_1 + M_2)/M$, $l = (M_1 - M_2)/M$, M_1 and M_2 are the magnetic moments of the sublattices whose moduli are $M/2$, h is the high-frequency field with the components

$$h_x = h_0 \cos \omega t, \quad h_y = h_0 \sin \omega t, \quad h_z = 0. \quad (\text{D.27})$$

If $h = 0$, then at equilibrium $m = 0$, $l_x = l_y = 0$, $l_z = 1$ (i.e., the Z axis is the antiferromagnetic axis), provided $A > 0$ and $b < 0$.

We shall determine first, in the linear approximation, the transverse components of the magnetic moments M_j ($j = 1, 2$) due to the high-frequency field (D.27), from the equations of motion

$$M_j = -\gamma [M_j \cdot H_j], \quad (\text{D.28})$$

where $H_j = -d\Phi/dM_j$. Conventional calculations yield the following resonance formulas for the cyclic variables $M_j^\pm = M_{jx} \pm iM_{jy}$:

$$M_{1,2}^\pm = \frac{\gamma M (\omega \pm \gamma H_A) h_0}{2(\omega_0^2 - \omega^2)} e^{i\omega t}, \quad M_{1,2}^\mp = \frac{\gamma M (\omega \pm \gamma H_A) h_0}{2(\omega_0^2 - \omega^2)} e^{-i\omega t}, \quad (\text{D.29})$$

where $\omega_0 = \gamma \sqrt{H_E H_A}$ is the resonance frequency, $H_E = (A - b)/M$ is the "exchange" field, $H_A = |b|/M$ is the magnetic anisotropy field.

To allow for the finite resonance linewidth $\Delta\omega$, it is necessary to carry out the substitution $\omega_0 \rightarrow \omega_0 - i\Delta\omega/2$ in M_j^+ and $\omega_0 \rightarrow \omega_0 + i\Delta\omega/2$ in M_j^- of (D.29).^{*} Using the formulas obtained in this way and the approximate inequalities

$$M_{1z} \simeq \frac{M}{2} - \frac{M_{1x}^2 + M_{1y}^2}{M}, \quad M_{2z} \simeq -\frac{M}{2} + \frac{M_{2x}^2 + M_{2y}^2}{M},$$

we can easily find the longitudinal magnetization $M_z = M_{1z} + M_{2z}$ which appears in the second (nonlinear) approximation. For the resonance frequency $\omega = \omega_0$, we have**

$$m_z = \frac{M_z}{M} = -\left(\frac{H_A}{H_E}\right)^{1/2} \left(\frac{h_0}{\Delta H}\right)^2,$$

where $\Delta H = \Delta\omega/\gamma$.

Thus, as in the case of ferromagnets, we must have crystals with a sufficiently narrow resonance line in order to observe this effect. Here, the coefficient $(H_A/H_E)^{1/2}$ is small compared with (D.26) but the quantity of interest to us (m_z) may be measured with a "zero" background while in the case of ferromagnets there is a strong background of spontaneous magnetization.

^{*}In the frequency region near resonance, this represents an addition to the right-hand part of (D.3) of the damping terms, for example, in the form $-M_j/\tau$, where $\tau = 2/\Delta\omega$. It is known that near resonance the shape of resonance curves is not very sensitive to the form of the damping terms in the equations of motion.

^{**}In the presence of a steady longitudinal field $H_z = H \ll \sqrt{H_E H_A}$ the value of M_z defined by this formula occurs side by side with the magnetization $\chi_{\parallel} H$, due to this field.

IV. REFINED CALCULATION OF THE TEMPERATURE DEPENDENCE OF χ_{\perp}

To illustrate such calculations, we shall consider the (z/\perp) for which $l \perp H$, and $m \parallel H \parallel Z$. The value of m will be found by a self-consistent method from the condition for a minimum value of the thermodynamic potential $\Omega = \mathcal{H}_0 + \Omega_s$, assuming that the spin-wave energy depends on m as a parameter.

From the general formula (D.5) with the condition $\cos \theta = 0$, we obtain

$$\varepsilon_k^{(1,2)} = [(\alpha \pm \alpha_3)^2 - (\beta \pm \beta_3)^2]^{1/2},$$

where

$$\begin{aligned} \alpha &= \left(\frac{\mu}{2M_0}\right) \left[A + A_k - B_k - 2m^2 (A + a) + \right. \\ &\quad \left. + \frac{1}{2} (1 - m^2) (a + b) - 2mh \right], \\ \beta_3 &= \left(\frac{\mu}{2M_0}\right) \left[(1 - m^2) (A + A_k - B_k) - \frac{1}{2} (1 - m^2) (a - b) \right], \\ \alpha_3 &= \left(\frac{\mu}{2M_0}\right) \left[m^2 (A + A_k - B_k) - \frac{1}{2} (1 - m^2) (a - b) \right], \\ \beta &= - \left(\frac{\mu}{2M_0}\right) (1 - m^2) (a + b). \end{aligned}$$

Approximately, bearing in mind that $A \gg A_k, B_k, a, b$, we can rewrite ε_{1k} and ε_{2k} in the form

$$\varepsilon_{1k} = \left(\frac{\mu}{M_0}\right) [AB_k + Ab + mh (A + A_k + B_k) + m^2 A (A - 2B_k)]^{1/2}, \quad (\text{D.30})$$

$$\varepsilon_{2k} = \left(\frac{\mu}{M_0}\right) [AB_k + mh (A + A_k + B_k) - m^2 A (A + A_k + 2B_k)]^{1/2}.$$

The thermodynamic potential is

$$\Omega = \frac{1}{2} (A + a) m^2 - mh + \kappa T \sum_{j,k} \ln (1 - e^{-\varepsilon_{jk} \kappa T}). \quad (\text{D.31})$$

Assume first that

$$\kappa T \gg \varepsilon_{10} \text{ and } \varepsilon_{20}.$$

From the condition $\partial \Omega / \partial m = 0$ we find for this case

$$m = \frac{h}{A} \left[1 + \frac{\pi^2}{30} \frac{3I^2 - I_A^2}{IA} \left(\frac{\kappa T}{I} \right)^4 \right], \quad (\text{D.32})$$

where

$$I_A^2 = \left(\frac{\mu}{M_0}\right)^2 \frac{AA_k}{k^2}.$$

Substituting into (D.31) the equilibrium value of m found in this way, we can calculate the magnetization

$$M_z(T, H) = -\frac{\partial \Omega}{\partial H}.$$

Finally, we have

$$M_z(T, H) = \chi_{\perp}(T) H,$$

where

$$\chi_{\perp}(T) = \chi_{\perp}(0) \left[1 - \frac{1}{4} \frac{\alpha}{\chi_{\perp}(0)} T^2 + \frac{\pi^2}{15} \frac{l^2 - l_A^2}{lA} \left(\frac{\kappa T}{lA} \right)^4 \right]. \quad (\text{D.33})$$

A similar calculation may be carried out for the temperature range $\varepsilon_{10} \gg \kappa T \gg \varepsilon_{20}$. As a result of such a calculation we find

$$\chi_{\perp}(T) = \chi_{\perp}(0) \left[1 + \frac{\pi^2}{10} \frac{\alpha}{\chi_{\perp}(0)} T^2 \left(\frac{\kappa T}{\mu H_E} \right)^2 + \frac{\alpha^2 H_E T^4}{64 M_0 \chi_{\perp}(0)} \right]. \quad (\text{D.34})$$

Thus, in this case $\Delta \chi_{\perp}(T)$ varies as T^4 and χ_{\perp} increases with temperature.

V. SPIN-WAVE ENERGY (ORTHORHOMBIC CRYSTALS)

We shall calculate the spin-wave energy for an orthorhombic crystal in the $H \parallel l \parallel Z$ state. The energy density (4.4) for an orthorhombic crystal should, according to (4.85), differ from (4.4) by the presence of terms of the $\frac{1}{2} a_1 m_x^2 + \frac{1}{2} b_1 l_x^2$ type. It is easily found that the parameters α and β are altered, compared with their values in (D.7) for a uniaxial crystal, in the following way:

$$\begin{aligned} \alpha &= \left(\frac{\mu}{2M_0} \right) \left[A + A_k + B_k - 2b_3 + \frac{1}{2} (a_1 + b_1) \right], \\ \beta &= \left(\frac{\mu}{2M_0} \right) \frac{1}{2} (a_1 + b_1), \\ \alpha_3 &= \left(\frac{\mu}{2M_0} \right) \frac{1}{2} (a_1 - b_1), \\ \beta_3 &= \left(\frac{\mu}{2M_0} \right) \left[A + A_k - B_k + \frac{1}{2} (a_1 - b_1) \right]. \end{aligned} \quad (\text{D.35})$$

From the general formula (D.5) we obtain in this case ($\theta = m = 0$, $\alpha_{1,2} = \alpha \pm \mu H$, $\beta_1 = \beta_2 = \beta = \beta^*$, $\alpha_3 = \alpha_3^*$ и $\beta_3 = \beta_3^*$) we obtain

$$\begin{aligned} \varepsilon_k^{(1,2)} &= \{ \alpha^2 - \beta^2 + \alpha_3^2 - \beta_3^2 + \\ &+ (\mu H)^2 \pm \sqrt{(\alpha^2 - \beta_3^2)(\mu H)^2 + (\alpha \alpha_3 - \beta \beta_3)^2} \}^{1/2}. \end{aligned} \quad (\text{D.36})$$

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